



U.S. Department of Energy

Office of Science

Integrated Field-Scale Subsurface Research Challenge

Oak Ridge Field Research Center

**Multiscale Investigations on the Rates and Mechanisms of
Targeted Immobilization and Natural Attenuation of Metal,
Radionuclide and Co-Contaminants in the Subsurface
(ORIFC project briefing)**

Environmental Remediation Science Program

Oak Ridge National Laboratory

Argonne National Laboratory

Florida State University

Georgia Tech

Lawrence Berkeley National Laboratory

Stanford University

University of Oklahoma

University of Tennessee

**ERSP Annual PI Meeting
Lansdowne, Virginia
April 7-10, 2008**





- **Scientific and Technical Coordination:** Dave Watson (Field Research Manager, ORNL), Paul Bayer (DOE site manager), Phil Jardine (PI), in consultation with project scientific disciplines.
 - **Geophysics:** Susan Hubbard*, Ken Williams, J. Chen (LBNL), Greg Baker and David Gaines (UT), Les Beard (Battelle)
 - **Geochemistry:** Scott Brooks*, Brian Spalding, Juski Hortita, and Chuck Garten (ORNL), Ken Kemner and Shelly Kelly (ANL)
 - **Microbiology:** Joel Kostka* (FSU), Tony Palumbo, Chris Schadt and Tom Phelps (ORNL), Joe Zhou (OU).
 - **Biogeochemistry:** Craig Criddle* and Weimin Wu* (Stanford), Baohua Gu and Chris Schadt (ORNL)
 - **Hydrology:** Dave Watson* (ORNL), Jack Parker (ORNL/UT), Peter Kitanidis (Stanford)
 - **Numerical Modeling:** Jack Parker* (UT), Craig Brandt and Fan Zhang (ORNL), Peter Kitanidis (Stanford), Jian Luo (Georgia Tech)
 - **Data Management:** Craig Brandt* (ORNL)
- * Disciplinary lead



Presentation Outline

- ORIFC Objectives / Goals / Site Description
- ORIFC Approach (Tasks A – D)
- Year-1 Results and Path Forward

Watershed Characterization: Define flowpaths and heterogeneities that control the fate and transport of contaminant plumes

Quantifying Natural Attenuation Processes: Define and quantify natural attenuation rates & mechanisms for U, Tc, and co-contaminant NO₃ across the Bear Creek watershed

Targeted Immobilization Strategies: Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate) using coupled geochemical and microbial techniques

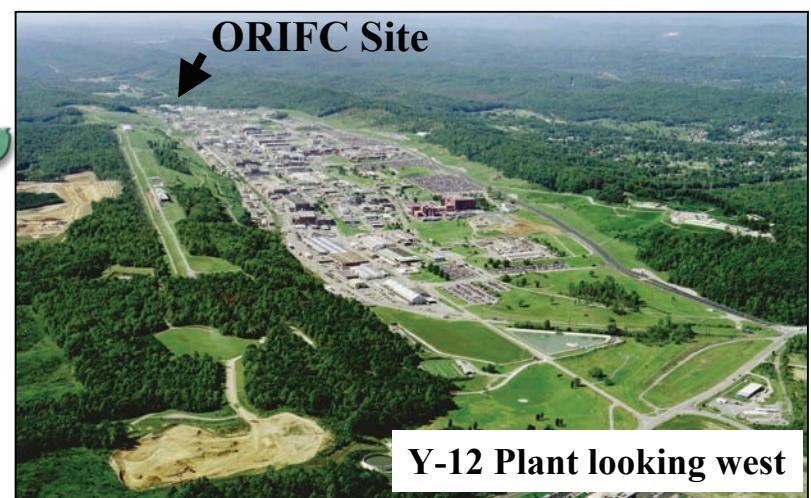
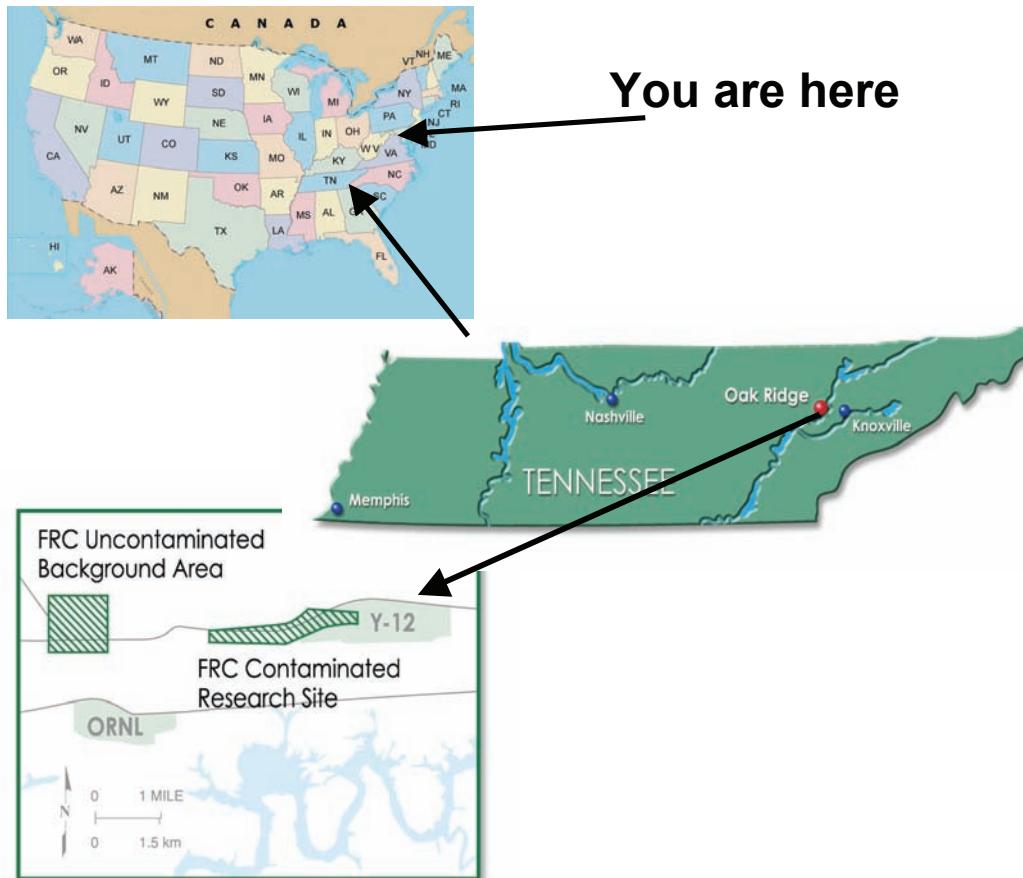
Multi-scale, Multi-process Modeling: Numerical modeling and data analysis from the molecular to the watershed scale

- Information Sources / Technology Transfer / Opportunities



Location

Oak Ridge Integrated Field-Scale Research Challenge





Site Description

The Oak Ridge IFC is located in eastern Tennessee

- contaminated and uncontaminated field facilities
- on-site and off-site laboratory facilities

At the contaminated site, unlined surface impoundments received acidic nitrate- and U-bearing waste from 1951 to 1983 at a rate of 2.5 million gallons/year

- Attempts were made to neutralize the waste and the ponds were capped as a parking lot in 1988

The region receives ~1400 mm rainfall / y with 10% contributing to groundwater recharge and 40% contributing to surface water recharge.

The subsurface media consist of fractured saprolite weathered from interbedded shale and limestone and is conducive to rapid preferential flow of water and solutes.

The matrix porosity serves as a "secondary contaminant source" whose aerial extent is massive (tens of kilometers).

Both aqueous and solid phase geochemistry and microbiology are spatially and temporally diverse.

The problem scale is both local and at the watershed level.



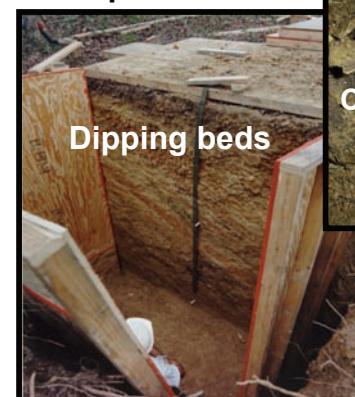
S-3 Ponds during denitrification



and after capping

ORNL media consisting of interbedded fractured weathered shales and limestone

Saprolite



Dipping beds



Close-up of saprolite (cm scale matrix blocks surrounded by fractures)

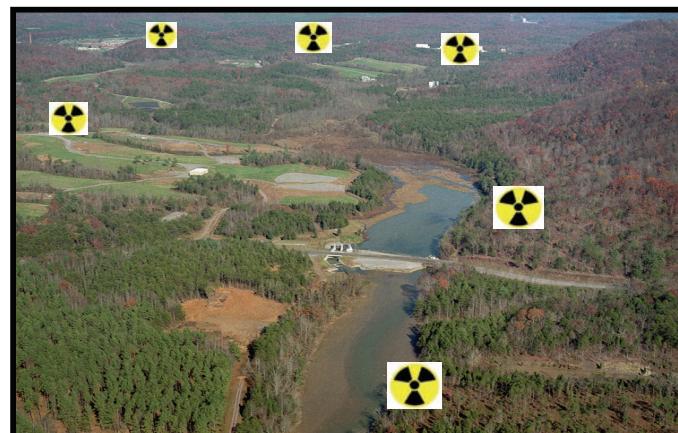
Underlying Bedrock





The problem is daunting due to its massive scale

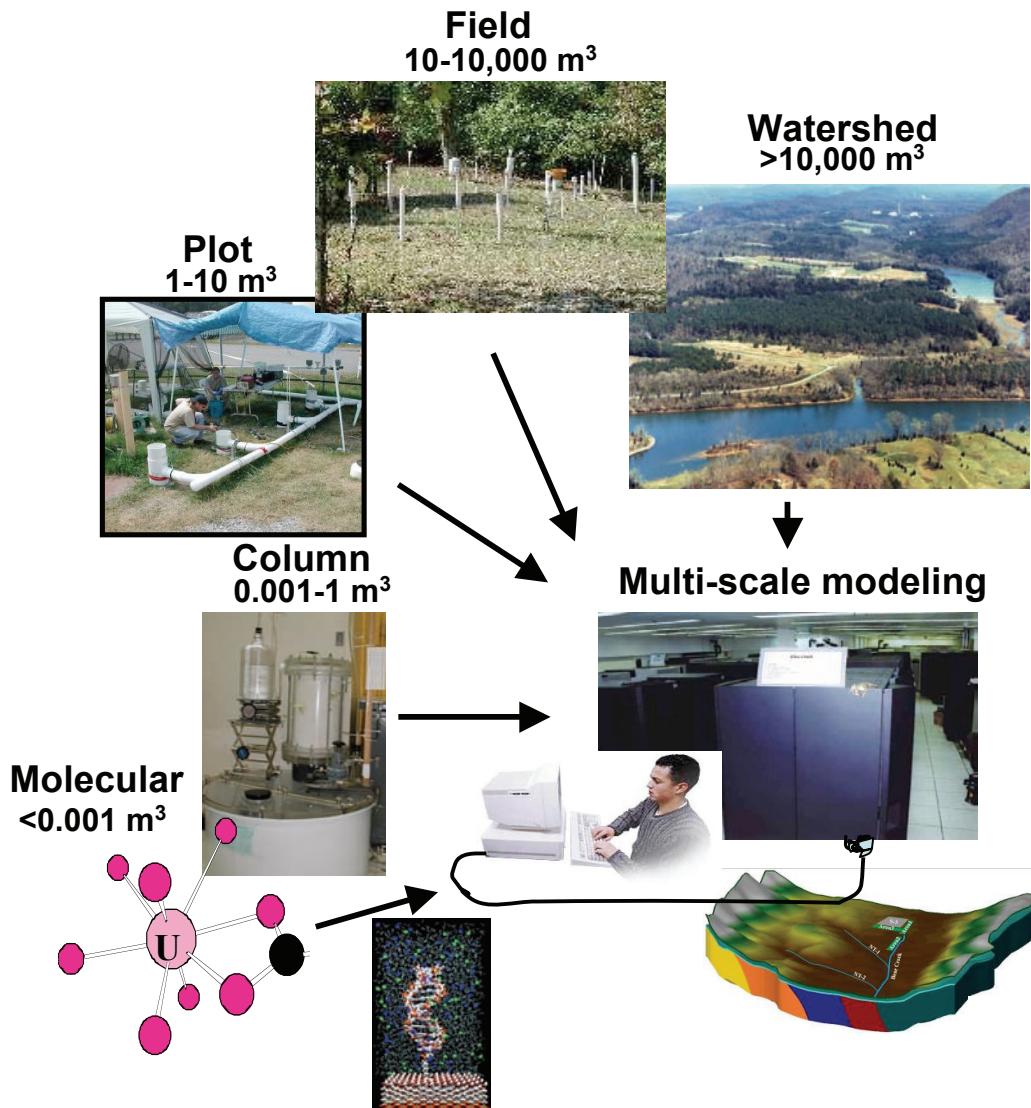
- No feasible removal or immobilization technologies for large volumes of contaminated subsurface saprolites, bedrock, groundwater.
- Decision has been made to leave contaminants in-place until remedial options are explored. Surface caps used to minimize water infiltration into primary waste ponds (contaminants continue to interact with the geosphere).
- Fundamental investigation, monitoring, and further evaluation of options
 - Natural physical attenuation via dilution by recharge or diffusion into high porosity, low permeability matrix.
 - Natural biogeochemical attenuation via sorption, redox transformation, degradation, dissociation, and precipitation reactions.
 - Targeted manipulations to convert metals and radionuclides to more stable forms.



Watershed scale
problem



ORIFC Project Goals



To advance the fundamental understanding and predictive capability of coupled processes that control *in situ* transport, remediation and natural attenuation of metals, radionuclides, and co-contaminants (i.e. U, Tc, NO₃)

- coupled hydrological, geochemical, and microbiological processes
- multiple scales ranging from molecular to watershed levels

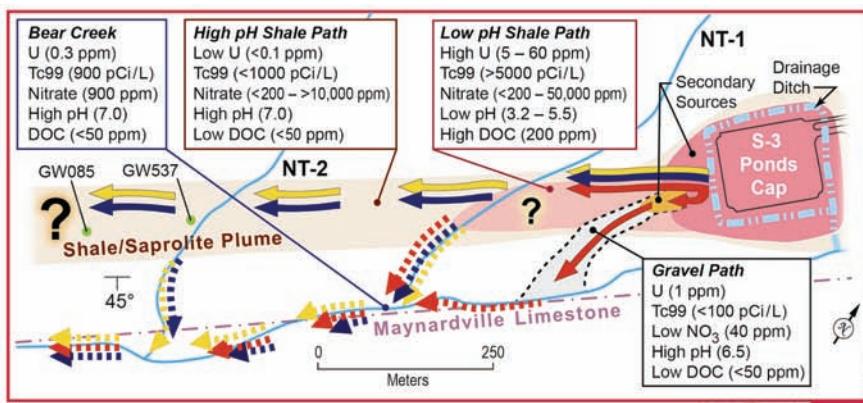
Provide multi-process, multi-scale predictive monitoring and modeling tools that can be used at the ORIFC site and throughout the DOE complex

- (1) inform and improve the technical basis for decision making
- (2) assess which sites are amenable to natural attenuation and which would benefit from source zone remedial intervention

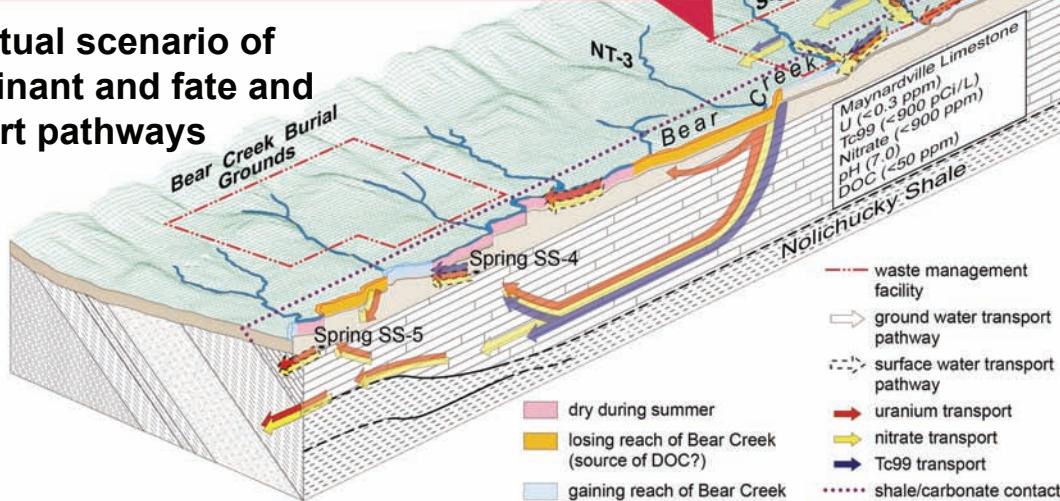


Focus on several secondary source zones and major flow pathways that represent a range of scales. These source zones and pathways contain numerous transition zones characterized by pronounced shifts in hydrology, geochemistry, and/or microbiology.

Multi-scale *in situ* research



Conceptual scenario of contaminant and fate and transport pathways



- (1) **S-3 Ponds secondary source (pH 3.2, GW U ~ 60 ppm, Solid U ~ 1000 ppm)**
- (2) **Carbonate gravel secondary source (pH 7.0, GW U ~ 1 ppm, Solid U ~ 14,000 ppm)**
- (3) **Low pH shale/saprolite pathway (strike parallel)**
- (4) **Neutral pH carbonate gravel pathway (engineered platform for tank farm)**
- (4) **Neutral pH Maynardville Limestone pathway (deep karst bedrock)**
- (6) **Recharge pathway (transient and spatially variable)**



Approach

Task A: Define flowpaths and heterogeneities that control the fate and transport of contaminant plumes

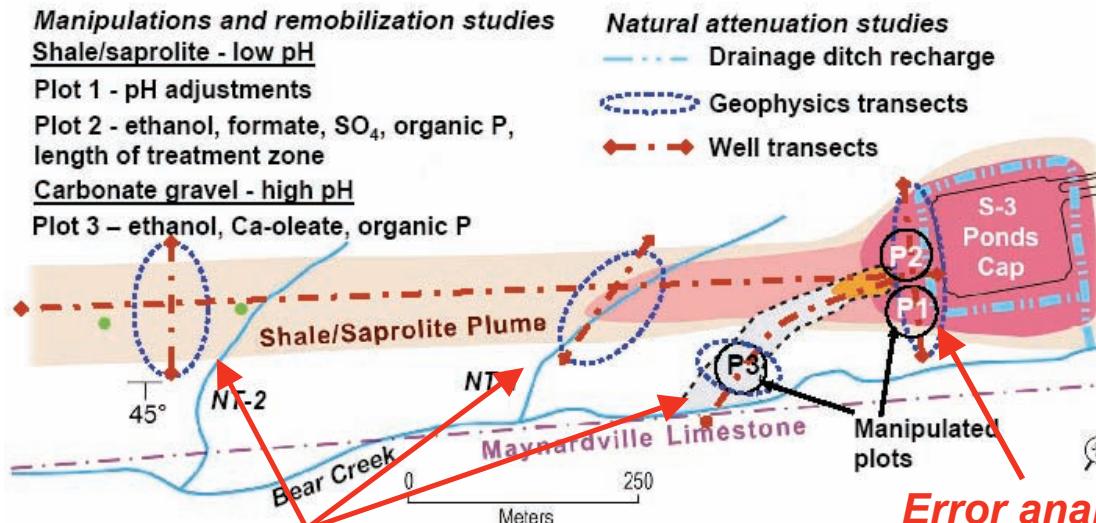
Link Geophysical Responses to Media Properties

- Development of geophysical-hydrogeochemical petrophysical relationships
- Assessing error associated with time-lapse geophysical datasets

Delineate Heterogeneity and Pathways

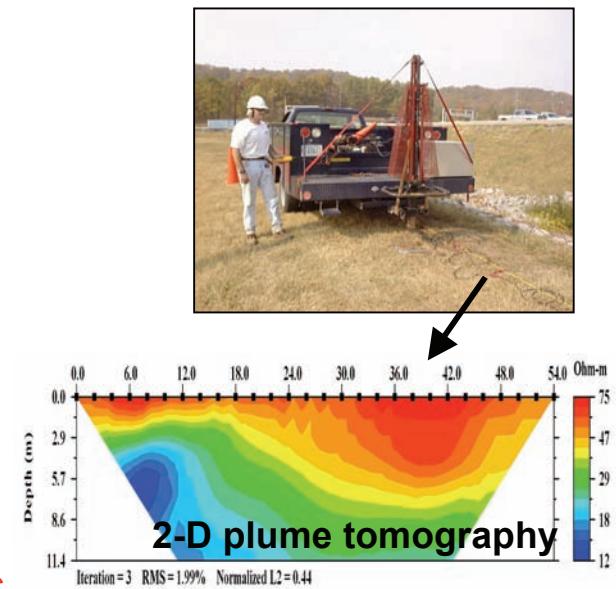
- Multi-scale 3-dimensional subsurface characterization using surface geophysics
- Development of joint inversion framework for watershed characterization

Example locations of research tasks at ORIFC site



*Acquisition of regional datasets
Plume characteristics / Media properties*

*Error analysis
Recharge studies*





Approach

Task B: Define and quantify natural attenuation rates & mechanisms across the Bear Creek watershed

- *Impacts of coupled pH, redox conditions, microbial activity, reactivity, etc. on U, Tc, and nitrate natural attenuation*
 - (isotopes, dissolved gases, PELCAPs, spatial and temporal variability along pathways and transition zones).
- *Impacts of recharge, antecedent moisture conditions on spatial and temporal plume dynamics*
 - (geochemistry, dilution, O₂, carbon source, microbial activity)

Location of research tasks at ORIFC site

Manipulations and remobilization studies

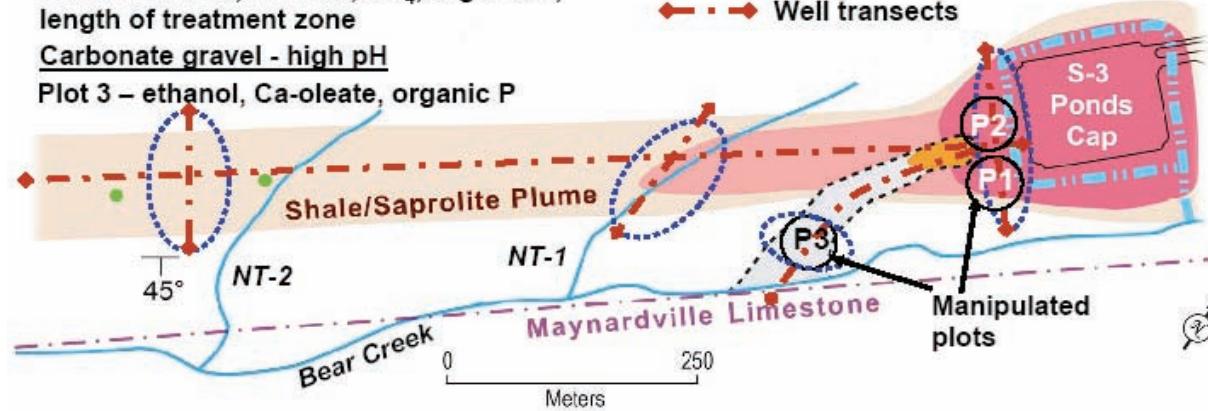
Shale/saprolite - low pH

Plot 1 - pH adjustments

Plot 2 - ethanol, formate, SO₄, organic P, length of treatment zone

Carbonate gravel - high pH

Plot 3 – ethanol, Ca-oleate, organic P

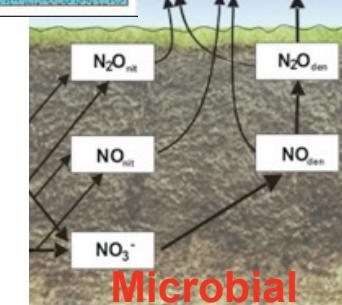
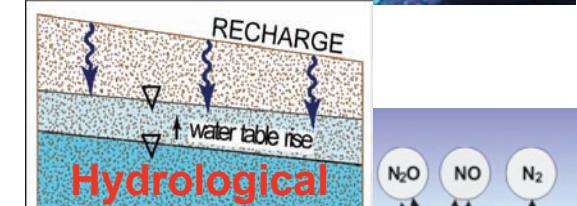
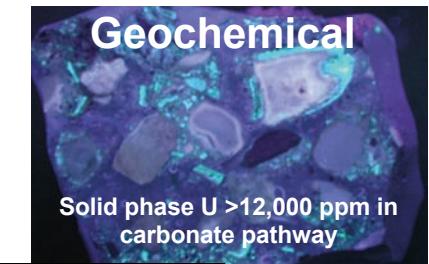


Natural attenuation studies

— Drainage ditch recharge

— Geophysics transects

— Well transects





Approach

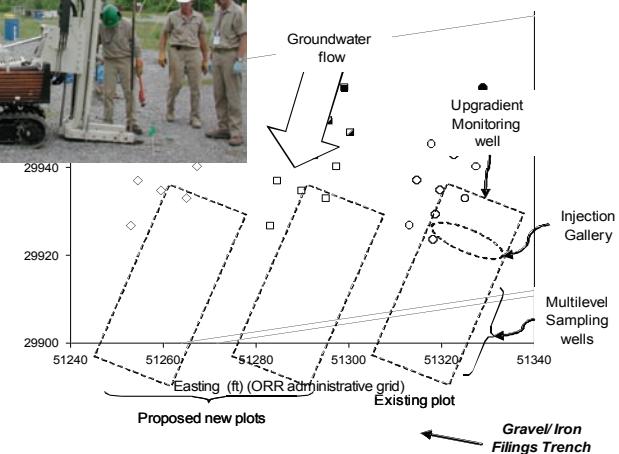
Task C: Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate)

Targeted manipulation experiments: (1) sustained bioreduction, (2) pH adjustment, (3) organo-phosphate amendments, (4) slow release electron donor amendments.

Monitor multi-scale hydrobiogeochemical and geophysical changes and propensity for contaminant remobilization.



Field plot manipulations

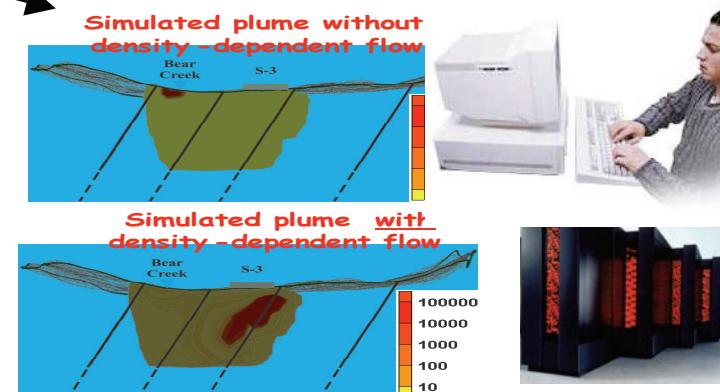


Task D: Multiprocess and multiscale numerical modeling and data analysis

Local plot scale and manipulation modeling (Tasks A and C results) and Advanced Pattern Recognition techniques (Task B results).

Site wide modeling (HydroBioGeoChem) / upscaling and model accuracy (Tasks A-C results, geophysics, hydro-bio-geochemical processes).

Multiprocess, multiscale computing





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- Information Sources / Technology Transfer / Opportunities



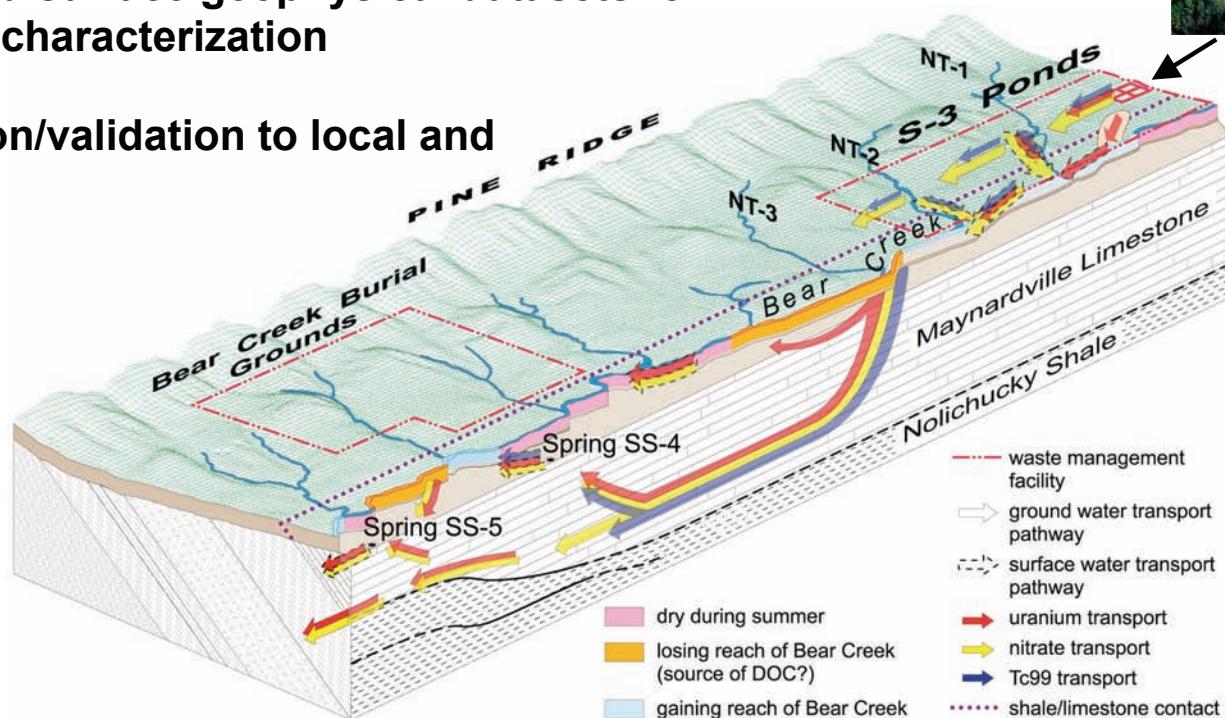
Watershed Characterization

Delineate Heterogeneity and Pathways Link Geophysical Responses to Media Properties

Quantify major contaminant flow paths and media heterogeneities to provide a framework for interpretation of large scale, spatially variable and transient processes

Development of a Bayesian approach to integrate multi-scale wellbore, crosshole, and surface geophysical datasets for quantitative watershed characterization

Provide parameterization/validation to local and site-wide models





Watershed Characterization

Regional Data Acquisition

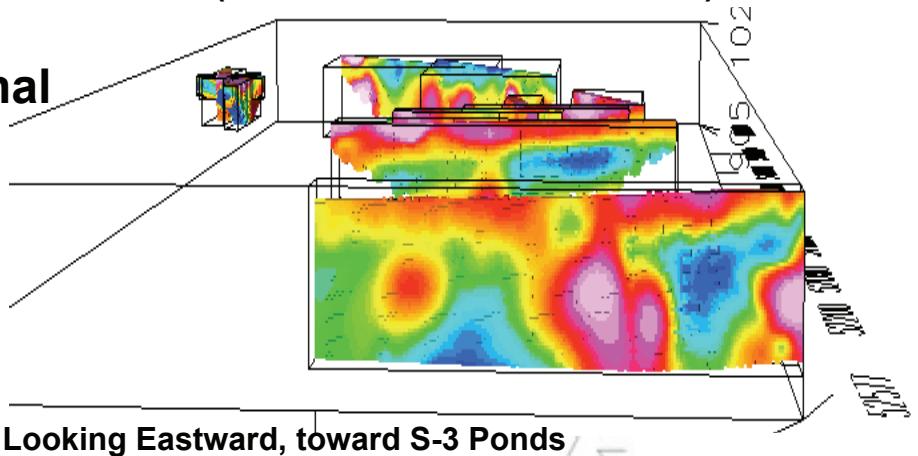
Surface geophysical data for 3-dimensional characterization of media properties and contaminant plumes

- Numerous coupled surface seismic refraction and electrical resistivity lines performed at various source areas, along plume transects, and the distal ends of plumes

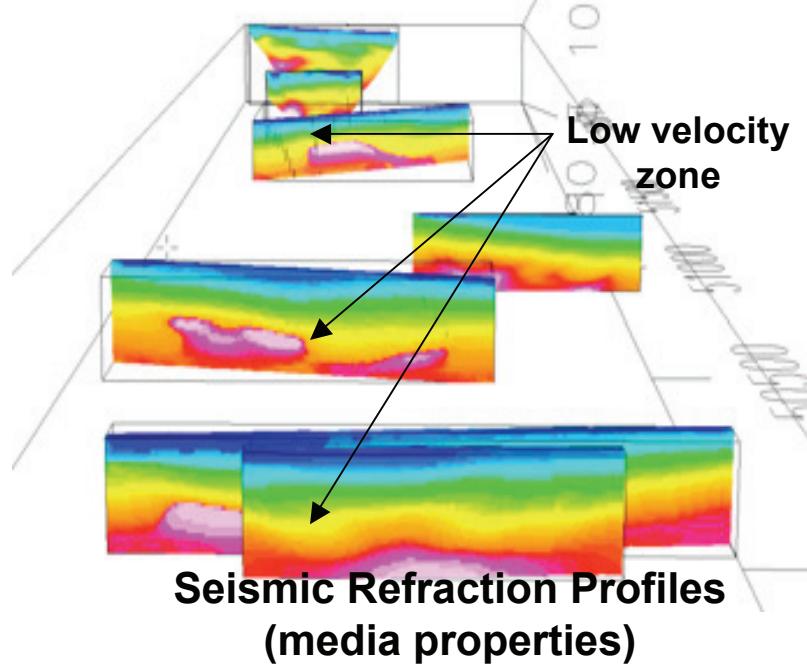
- Geophysical data being cross-correlated with traditional macroscopic measurements such as Geoprobe conductivity profiles, refusal, and water quality data



Electrical resistivity profiles
(contaminant concentration)



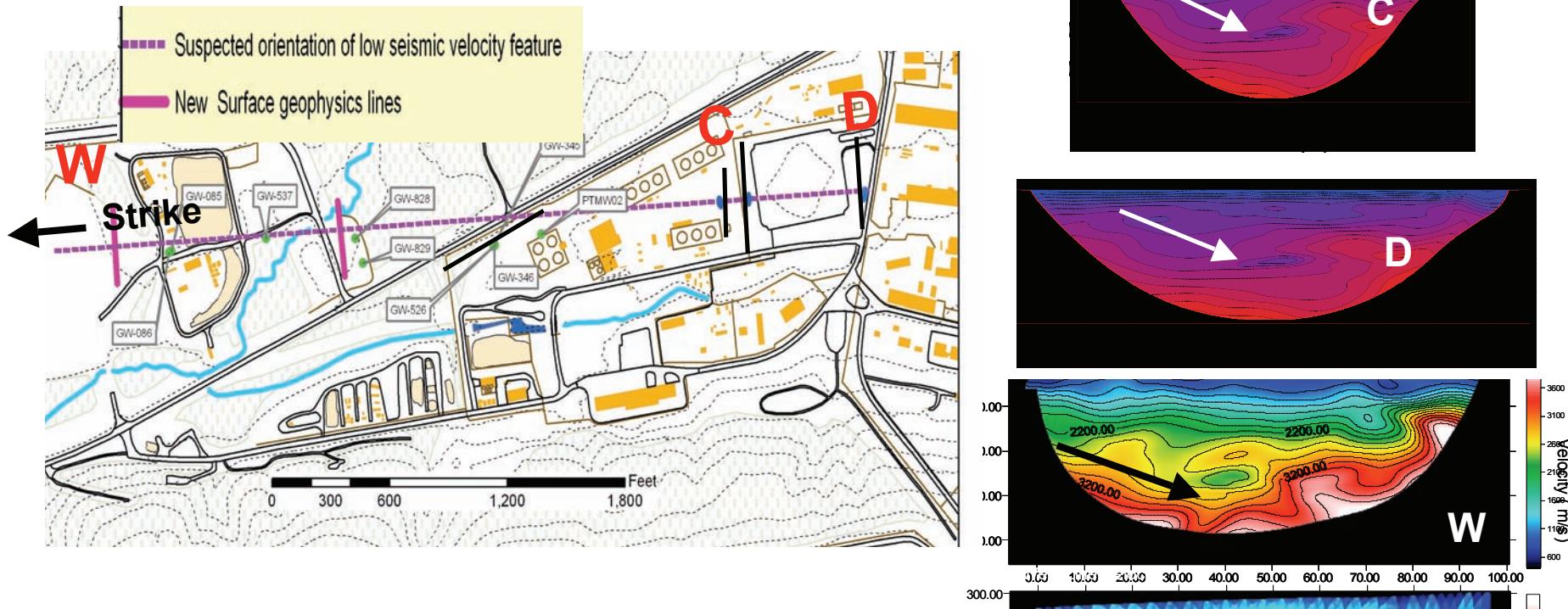
Looking Eastward, toward S-3 Ponds



Seismic Refraction Profiles
(media properties)



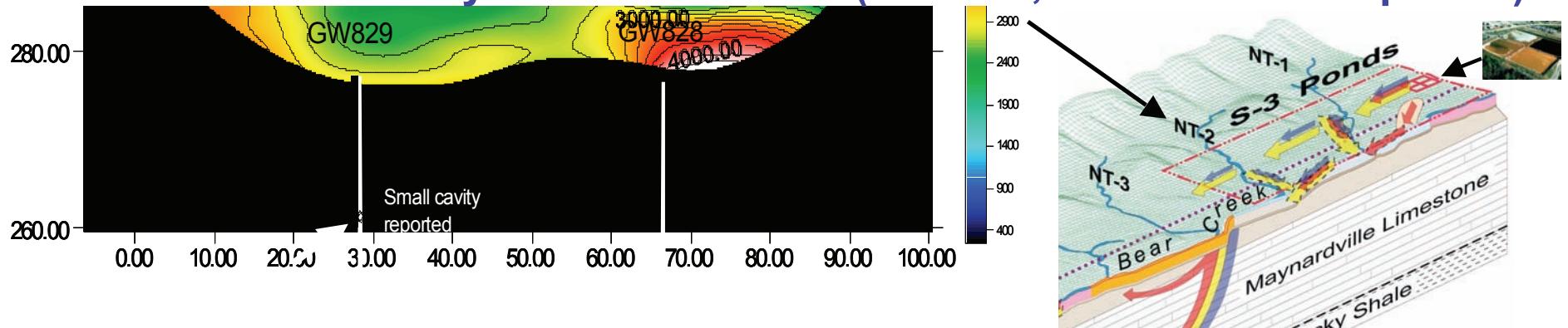
Origin of Low Velocity Anomaly: Seismic refraction profiles indicate an anomalous and laterally continuous north-dipping feature down the watershed providing confirmation of the utility of the geophysical technique to define lithologic features involved in contaminant transport



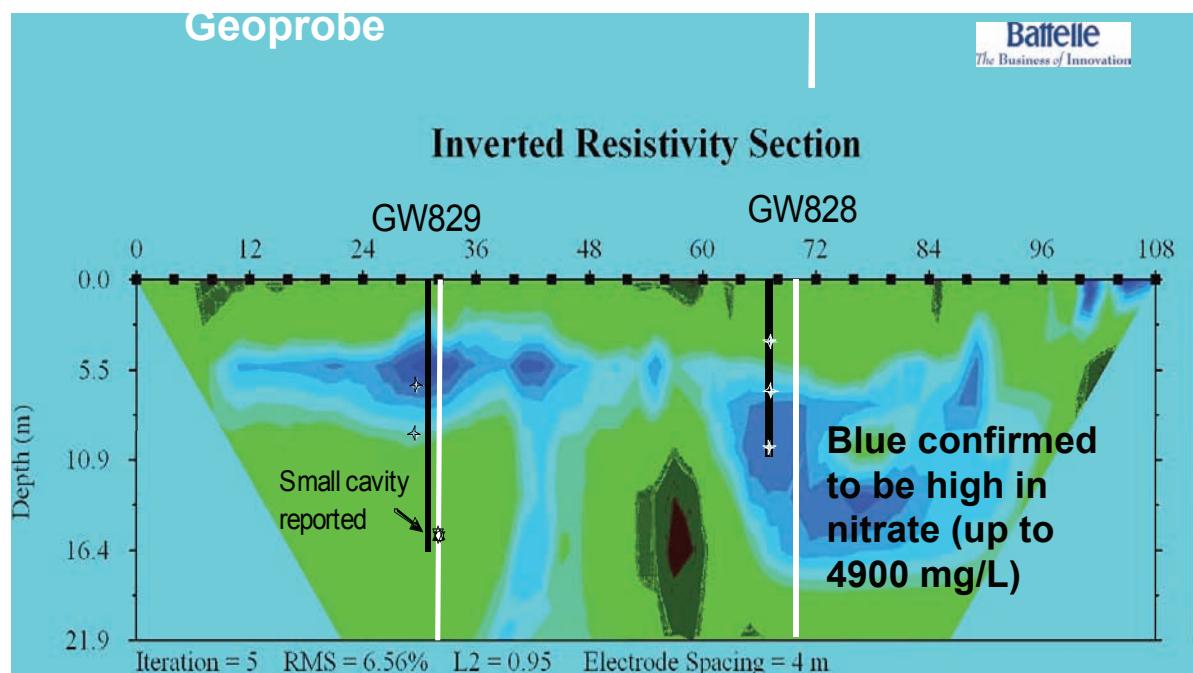
Surface seismic refraction data indicate the location of subsurface anomaly many Km down the valley – self replicating feature may be massive contaminant conduit



Seismic and resistivity sections at NT-2 (far-field, ~2 Km from S3 ponds)



As was noted near the source (Watson et al., 2005), groundwater quality and depth to refusal consistent with surface ERT and seismic geophysics, respectively



Suggests wide range utility of ERT for quantifying contaminant plumes at the watershed scale

Confirmed to be good targets for geophysics studies that collect time series data of recharge

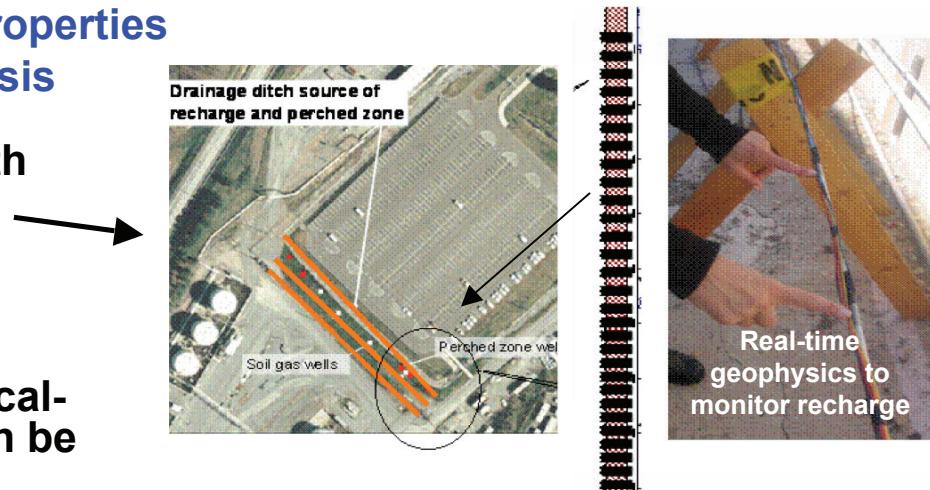


Linking Geophysical Response to Media Properties

Time-Lapse Geophysical Error Analysis

Understand inherent errors associated with acquisition and processing

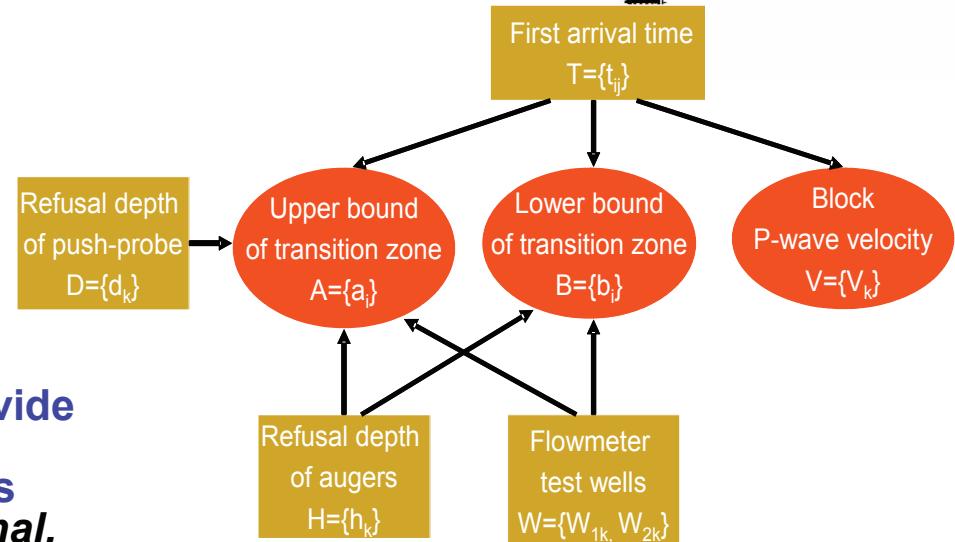
defining signals not associated with the process that we are attempting to monitor



Collection of hydrogeochemical-geophysical-microbiological datasets, which will in turn be used to develop site-specific, field-scale petrophysical relationships

Development of a Bayesian approach to integrate multi-scale wellbore, crosshole, and surface datasets

Extension of the approach with surface geophysical datasets is expected to provide insights into rates and mechanisms of geochemical and hydrological processes associated with natural episodic, seasonal, and annual recharge over field-relevant scales



An example of a Bayesian Estimation Framework incorporates surface seismic refraction arrival times and wellbore measurements (i.e., depth of refusal, flowmeter data) to estimate zonation at the watershed scale

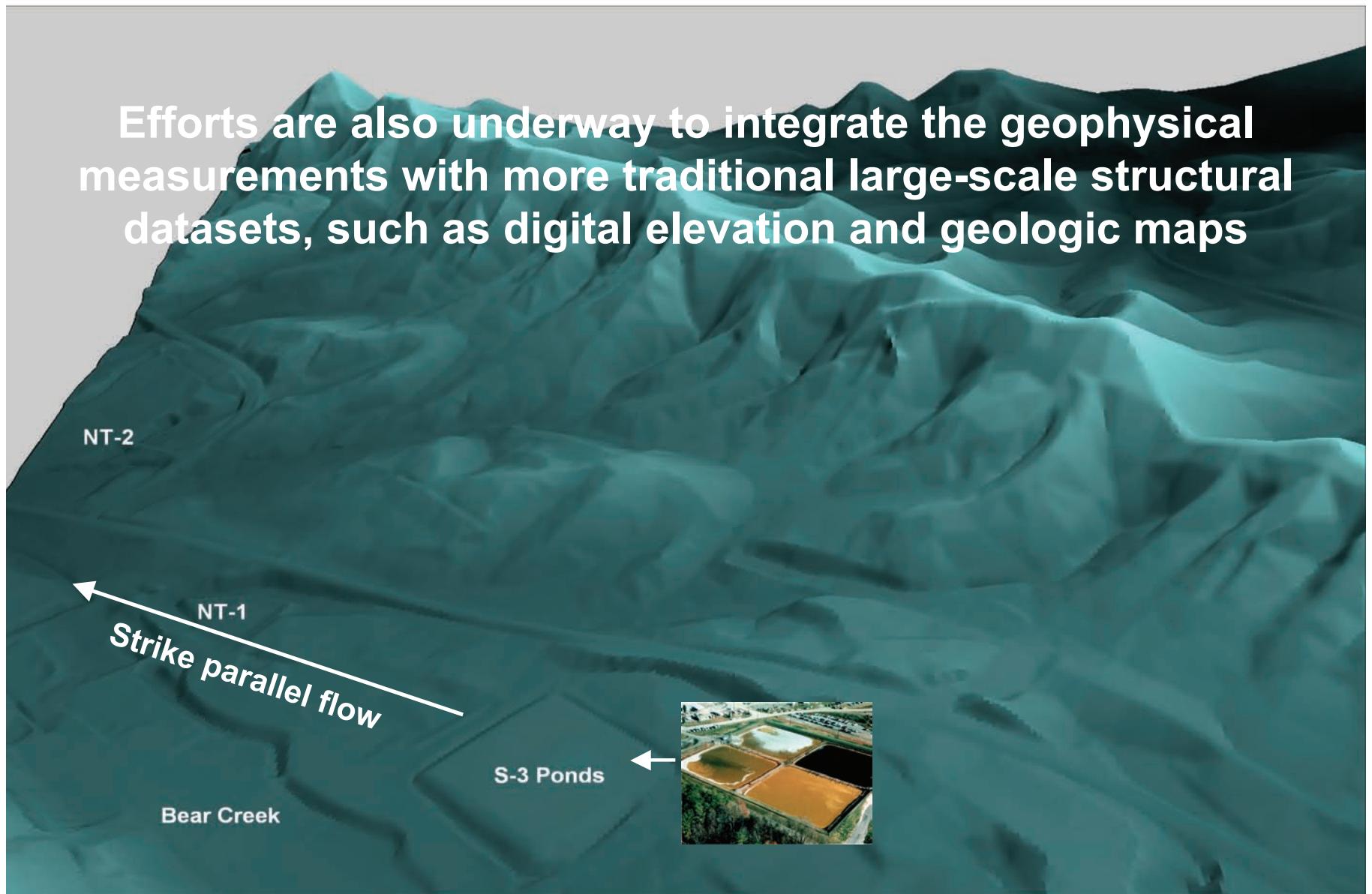


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INTEGRATED FIELD
RESEARCH CHALLENGE

Watershed Characterization



Efforts are also underway to integrate the geophysical measurements with more traditional large-scale structural datasets, such as digital elevation and geologic maps





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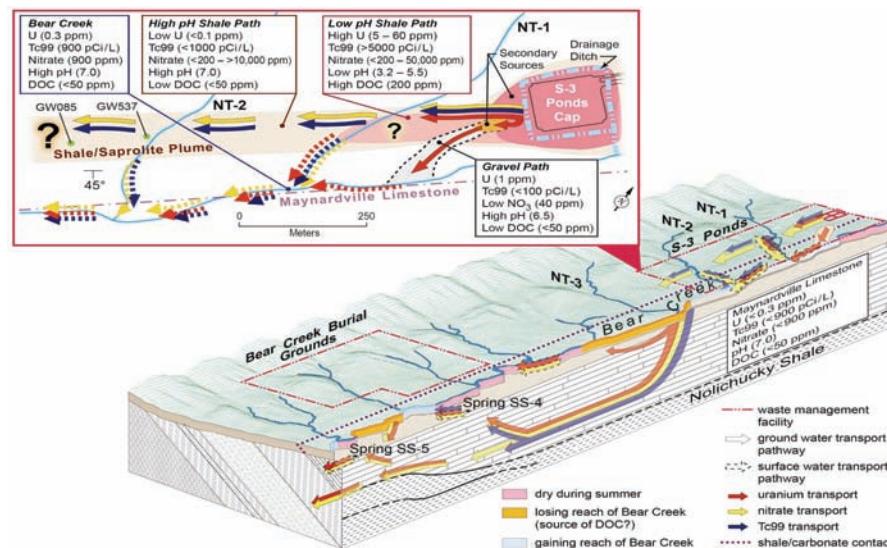
- Information Sources / Technology Transfer / Opportunities



Define and quantify natural attenuation rates & mechanisms across the Bear Creek watershed

Watershed scale databases that couple recharge, hydrologic drivers, geochemistry, and microbial activity on spatial and temporal plume dynamics (focus on U, Tc, and nitrate natural attenuation)

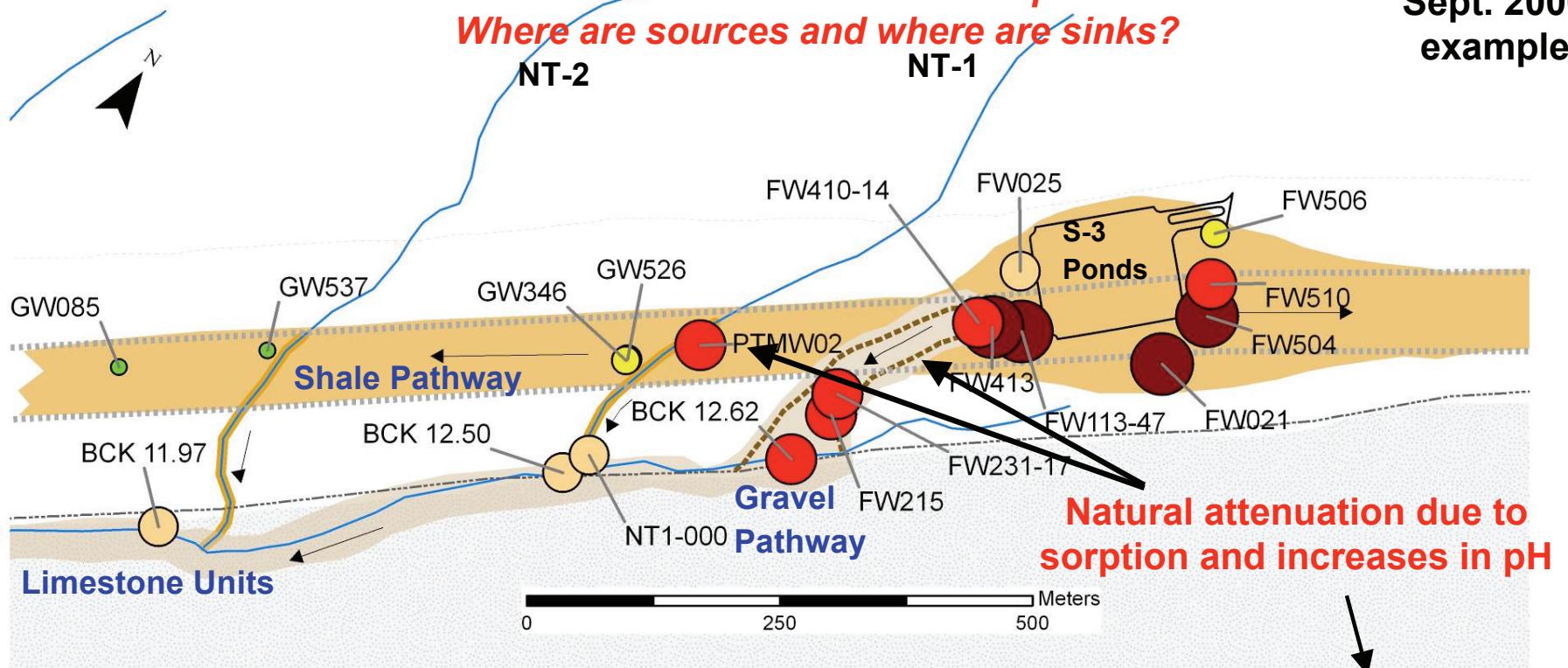
- focus on *rates and mechanisms* of sequestration / release in sources / sinks
- spatial and temporal *variability of coupled processes* along pathways and transition zones
- coupling measurement techniques (geophysics, isotopes, dissolved gases, PELCAPs)



Uranium Concentration Down the Valley

*What are the kinetics and mechanisms of uptake and release?
Where are sources and where are sinks?*

Sept. 2006
example



Legend

Uranium (mg/l)

- 0.00 - 0.02
- 0.03 - 0.10
- 0.10 - 0.50
- 0.50 - 10.00
- 10.00 - 100.00

→ Flow Direction

----- Carbonate Boundary

----- Units Line

----- Primary Shale Transport Zone

— Bear Creek

— S-3 Ponds

Plumes

Carbonate

Shale

Stratigraphy

Carbonate

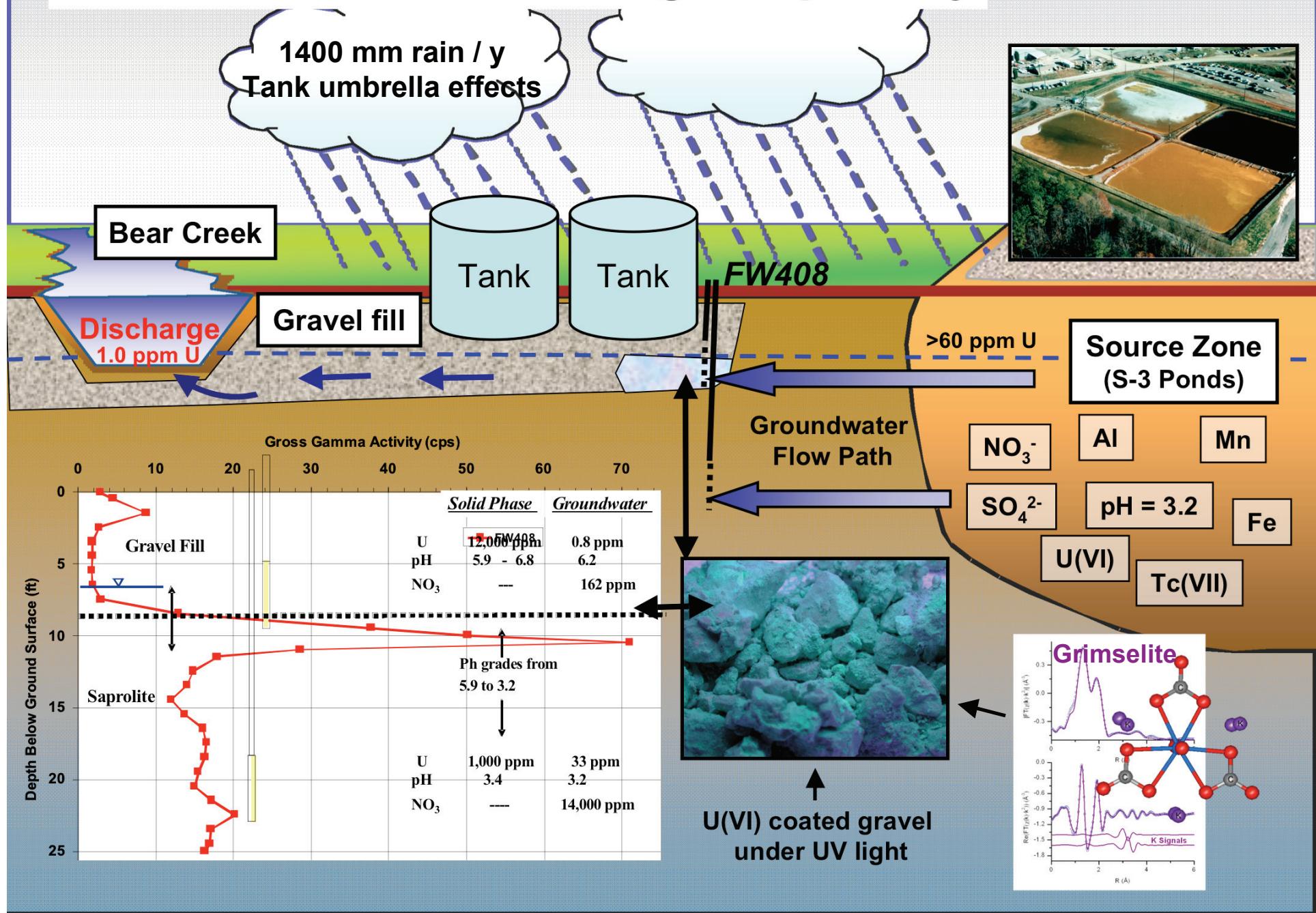
Shale

Uranium MCL = 0.03 mg/l



Geochemical attenuation

Uranium source / sink in the gravel pathway

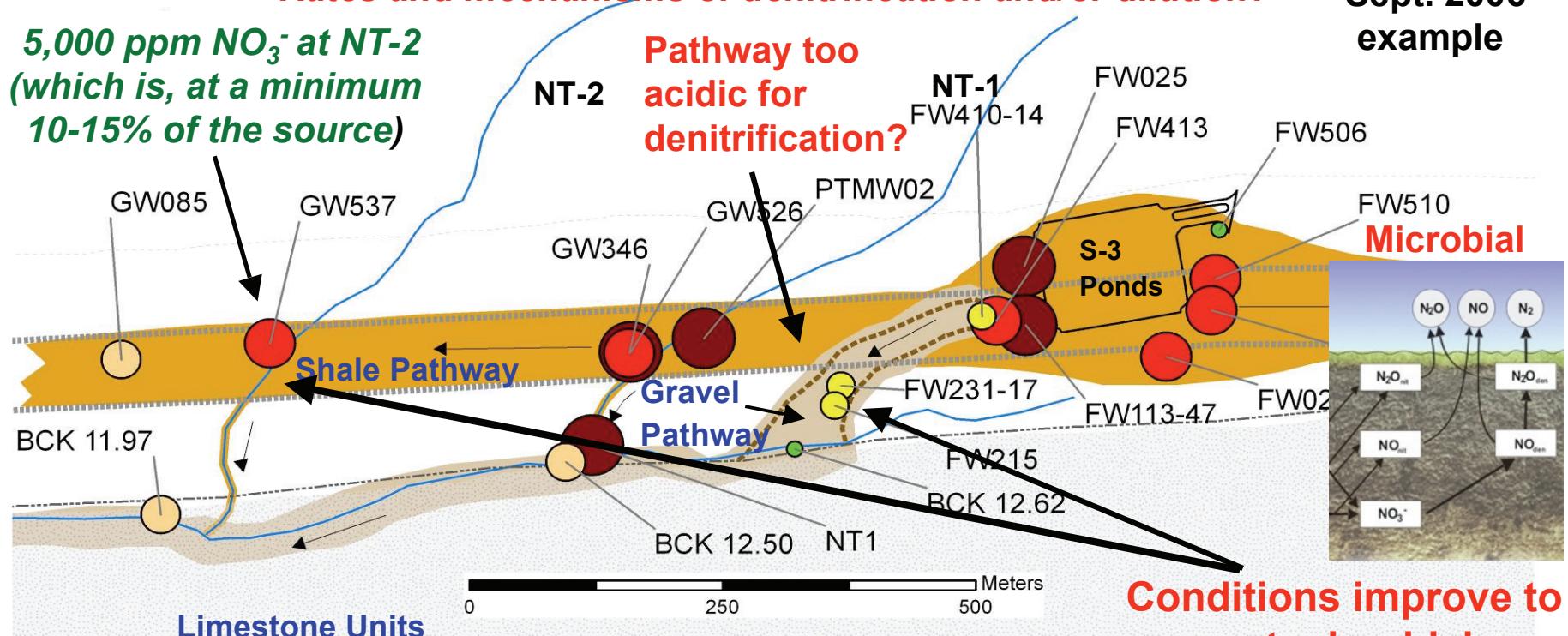


Nitrate Concentration Down the Valley

Rates and mechanisms of denitrification and/or dilution?

Sept. 2006
example

5,000 ppm NO_3^- at NT-2
(which is, at a minimum
10-15% of the source)



Conditions improve to support microbial activity (e.g. pH ~ 7). Indication of natural attenuation via denitrification?

Isotopes, N_2/Ar ratio, and coupled processes to the rescue

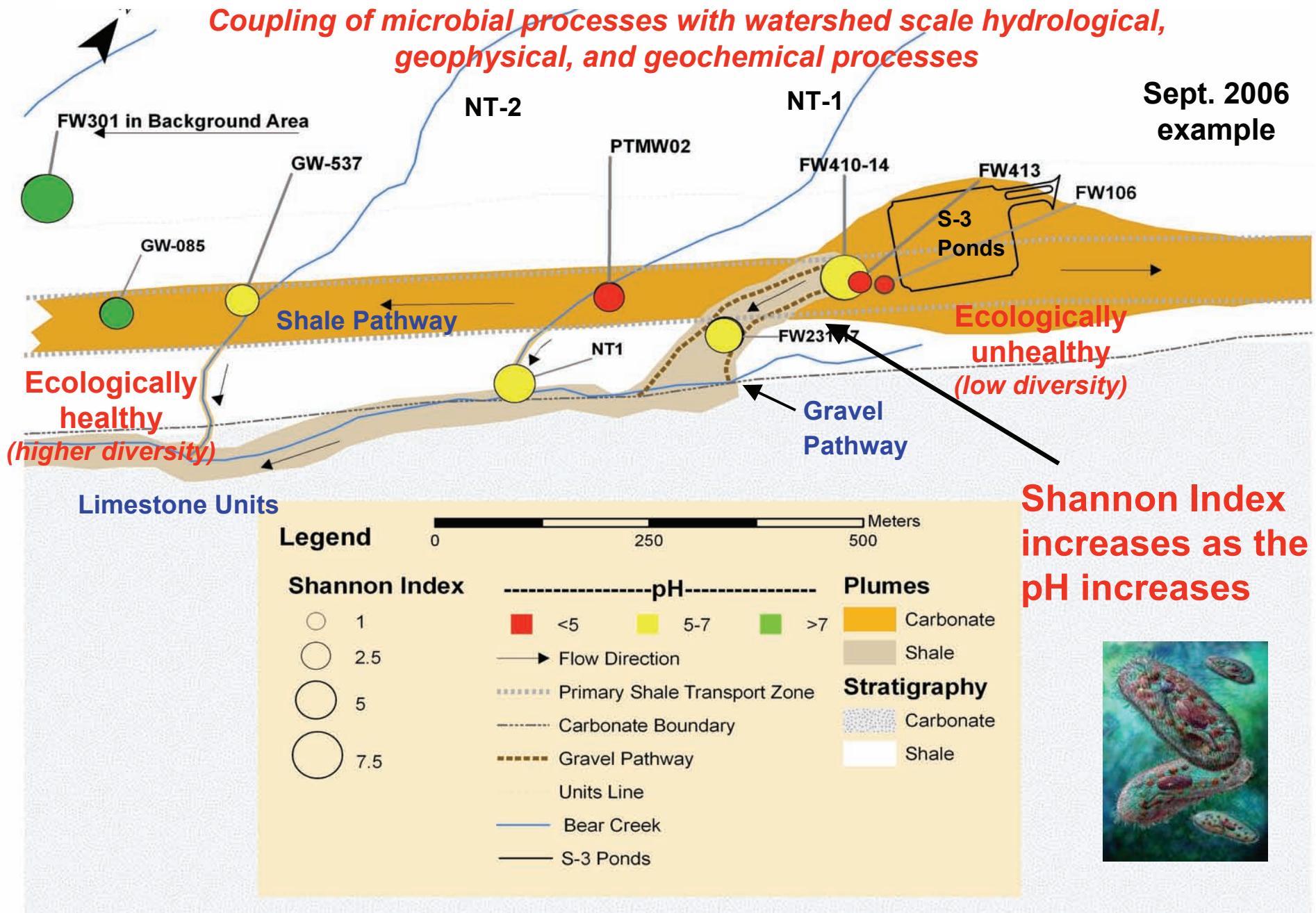
Legend

Nitrate (mg/l)	Stratigraphy
< 44	Bear Creek
44-150	Carbonate
150-1,000	Shale
1,000-10,000	Gravel Pathway
>10000	Primary Shale Transport Zone

Nitrate MCL = 10 mg/l

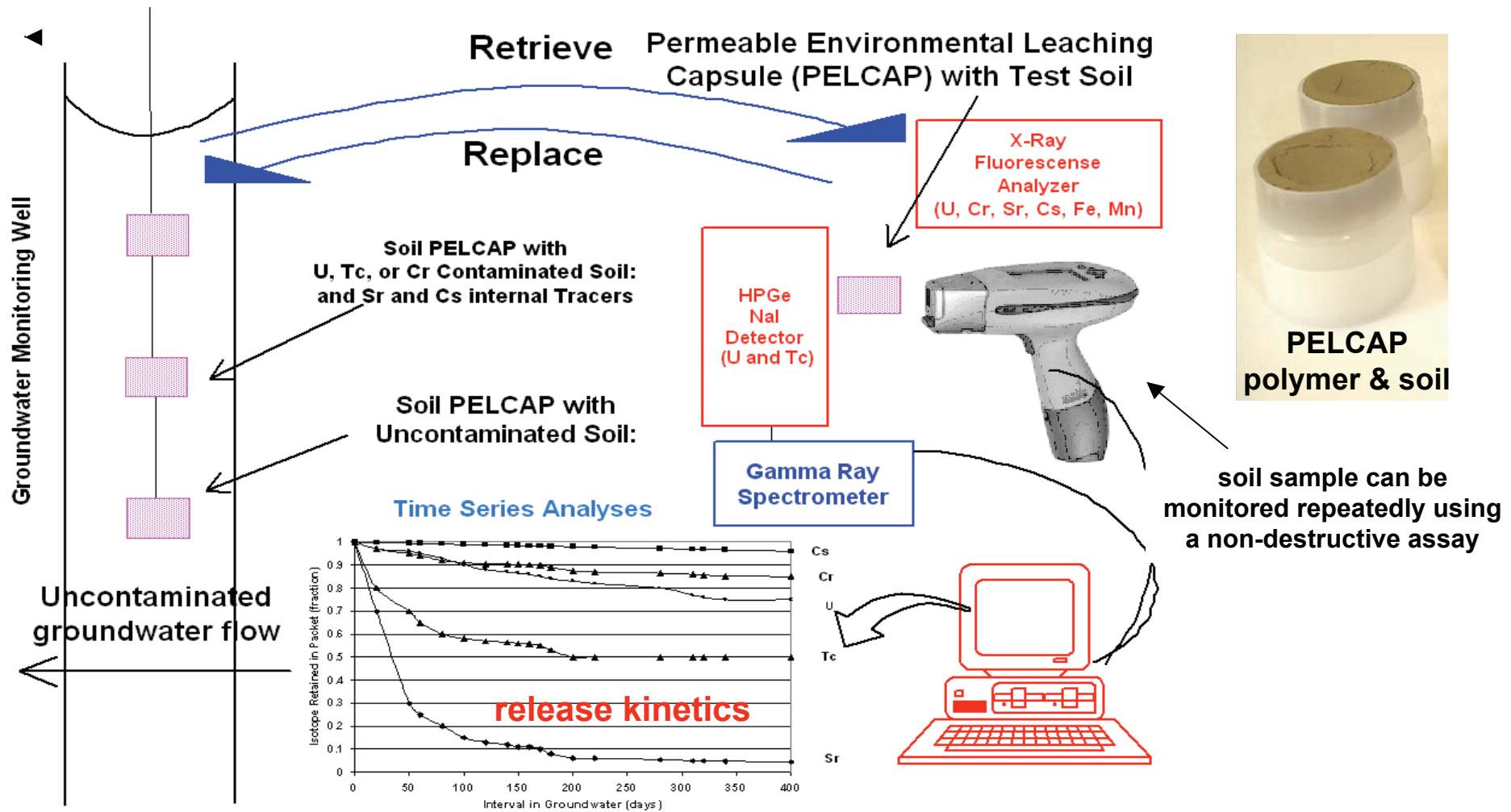
Shannon Index vs pH Down the Valley

Coupling of microbial processes with watershed scale hydrological, geophysical, and geochemical processes





Quantifying *In situ* Reactive Contaminant Behavior Across the Watershed Permeable Environmental Leaching Capsules (PELCAPs)





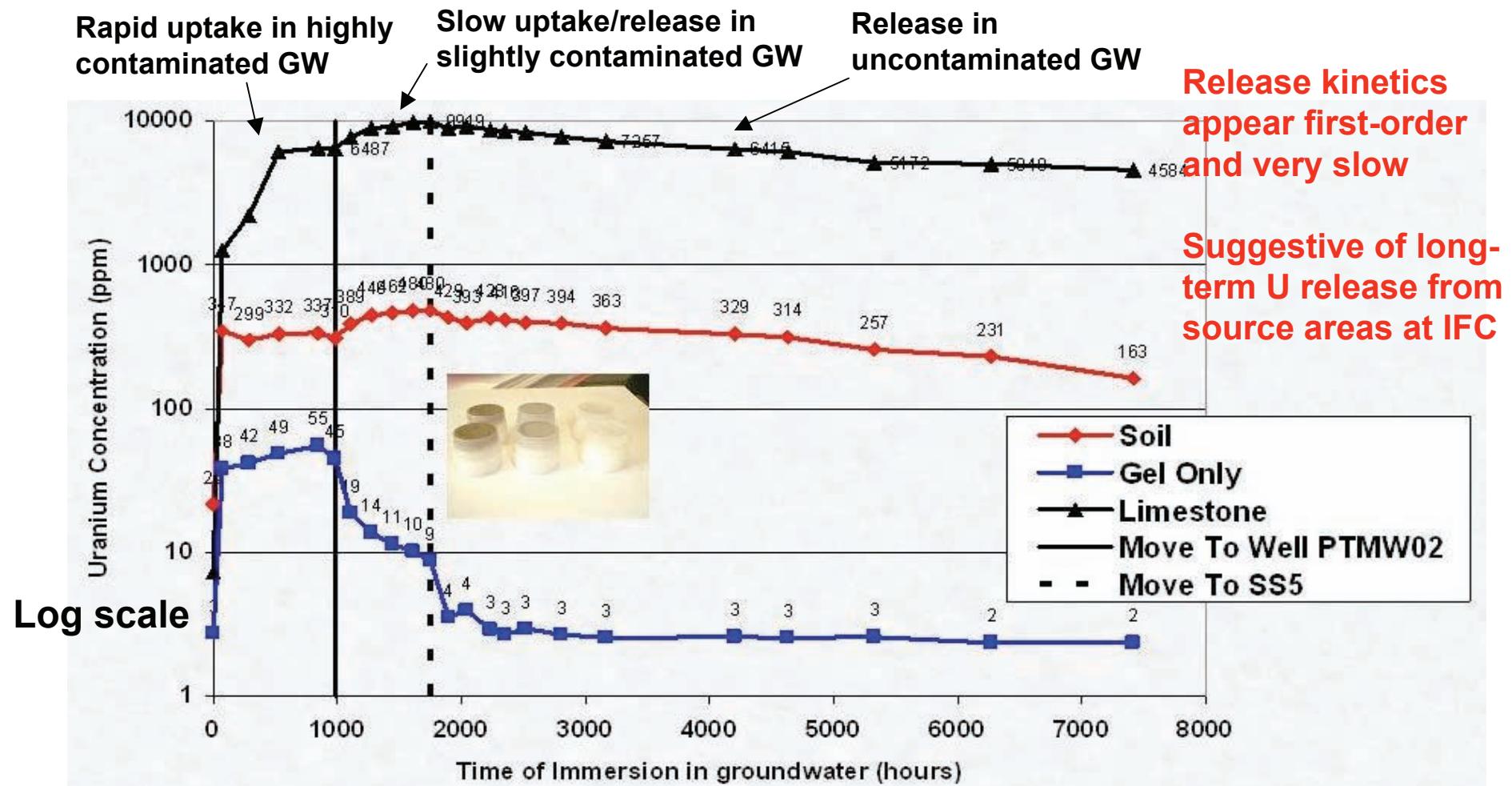
**OAK RIDGE
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RESEARCH CHALLENGE**

Natural Attenuation

PELCAPs



***In situ* uptake and release of U in ORIFC groundwater using the PELCAP methodology. Polymer-encapsulated soils behave very similarly to un-encapsulated soils with respect to U other inorganic ion interactions**





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RESEARCH CHALLENGE**

Natural Attenuation

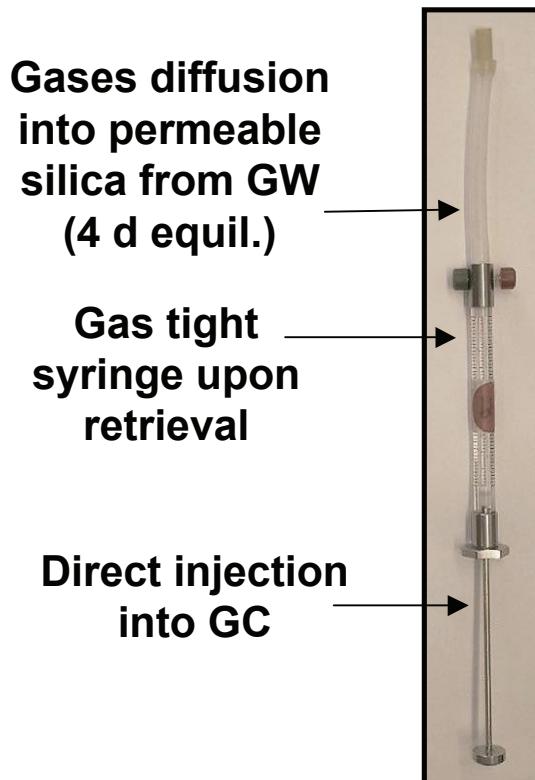
Dissolved Gases – unique method of tracking contaminant fate



Quantifying Dissolved Gas Species to Assess Contaminant Behavior Across the Watershed

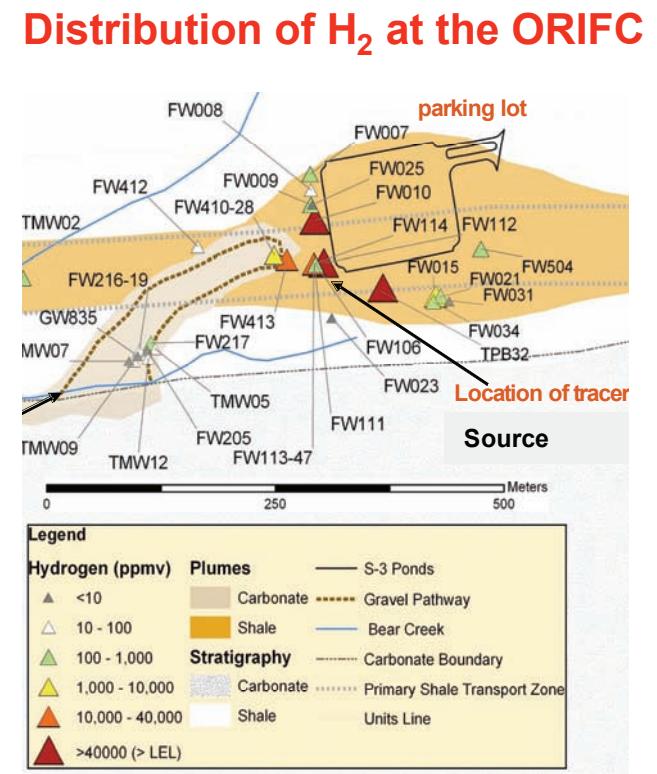
Technique involves passive gas diffusion into gas tight syringe sampler

This integrated fixed gas sampling and analysis protocol is unique and should greatly facilitate monitoring of fixed gases as indicators of microbial and chemical processes



Thousands of passively-collected samples at the ORIFC indicate an *unusual* average composition: 56% CO₂, 32.4% N₂, 2.6% O₂, 2.6% N₂O, 0.21% CH₄, 0.093% H₂, and 0.025% CO.

Quantitative assessment of microbial denitrification and substrate utilization byproducts.





Isotopic Signatures of Aqueous and Dissolved Gas Species to Assess Contaminant Behavior Across the Watershed

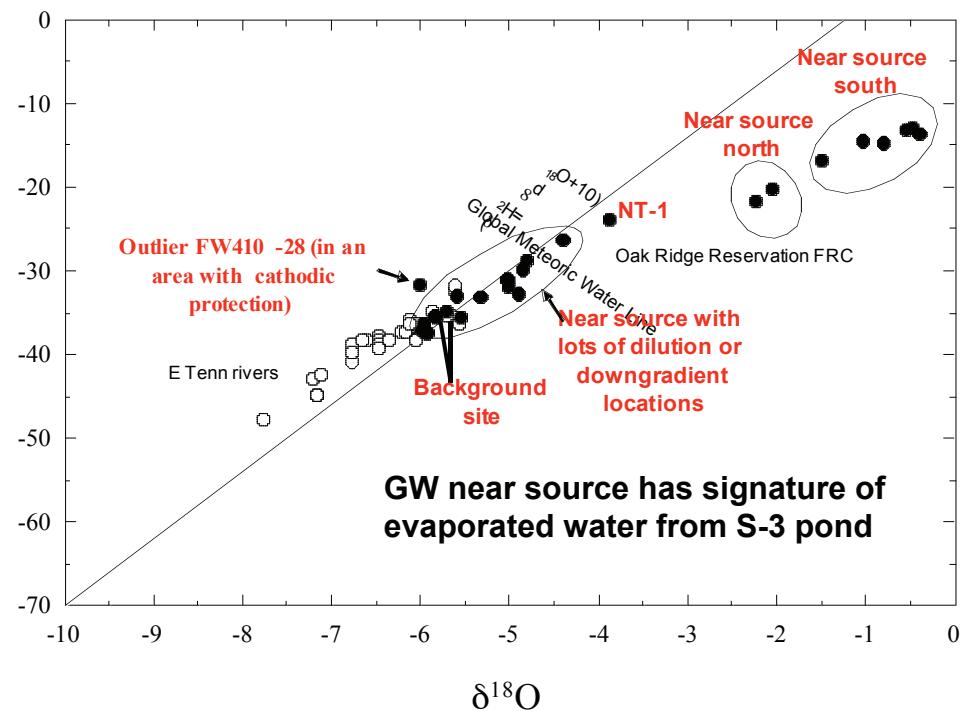
Quantify suite of stable isotope ratios in different solute and gaseous species within contaminant plumes of multiple scale

(e.g., $^{15}\text{N}/^{14}\text{N}$ in nitrate, N_2O , and N_2 ; $^{18}\text{O}/^{16}\text{O}$ in nitrate; $^2\text{H}/^1\text{H}$ in dissolved H_2 gas; and $^{13}\text{C}/^{12}\text{C}$ in acetate, citrate, natural DOC, CO_2 , and CH_4)

Target drastically different groundwater geochemistry to provide quantitative information on the *in situ* rates and mechanisms of nitrate natural attenuation and source identification in heterogeneous field-scale environments.

Several watershed-wide field sampling campaigns on >20 groundwater wells and numerous surface waters

- Geochemistry
- Dissolved gases
- Isotopes N,O,C,H
- N_2/Ar as bioindicator of denitrification
- Microbial characterization PCR
- Hg (related to new ORSFA)



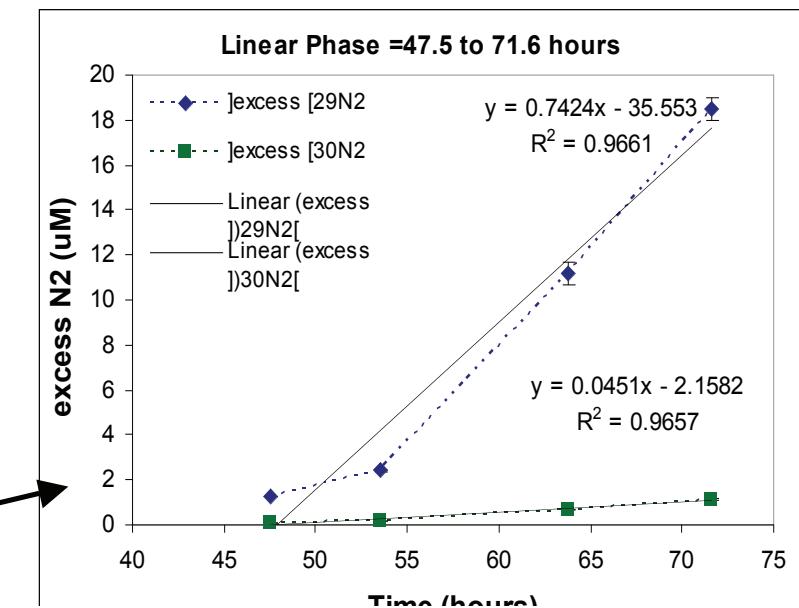


Watershed wide protocols

- Optimized and standardized common methods for groundwater and sediment sample collection, processing and nucleic acids extraction across labs on the team
- Development and standardization of common methods for qPCR across the team that allow for quantitative estimates of population numbers for important metal reducing FRC taxa (*Geobacter*, *Anaeromyxobacter* & others) and functional genes involved in processes of interest (*dsrA*, *gltA* and *nirK/S*)
- Development and testing of *tRFLP* methods for rapid screening of overall community diversity and activity

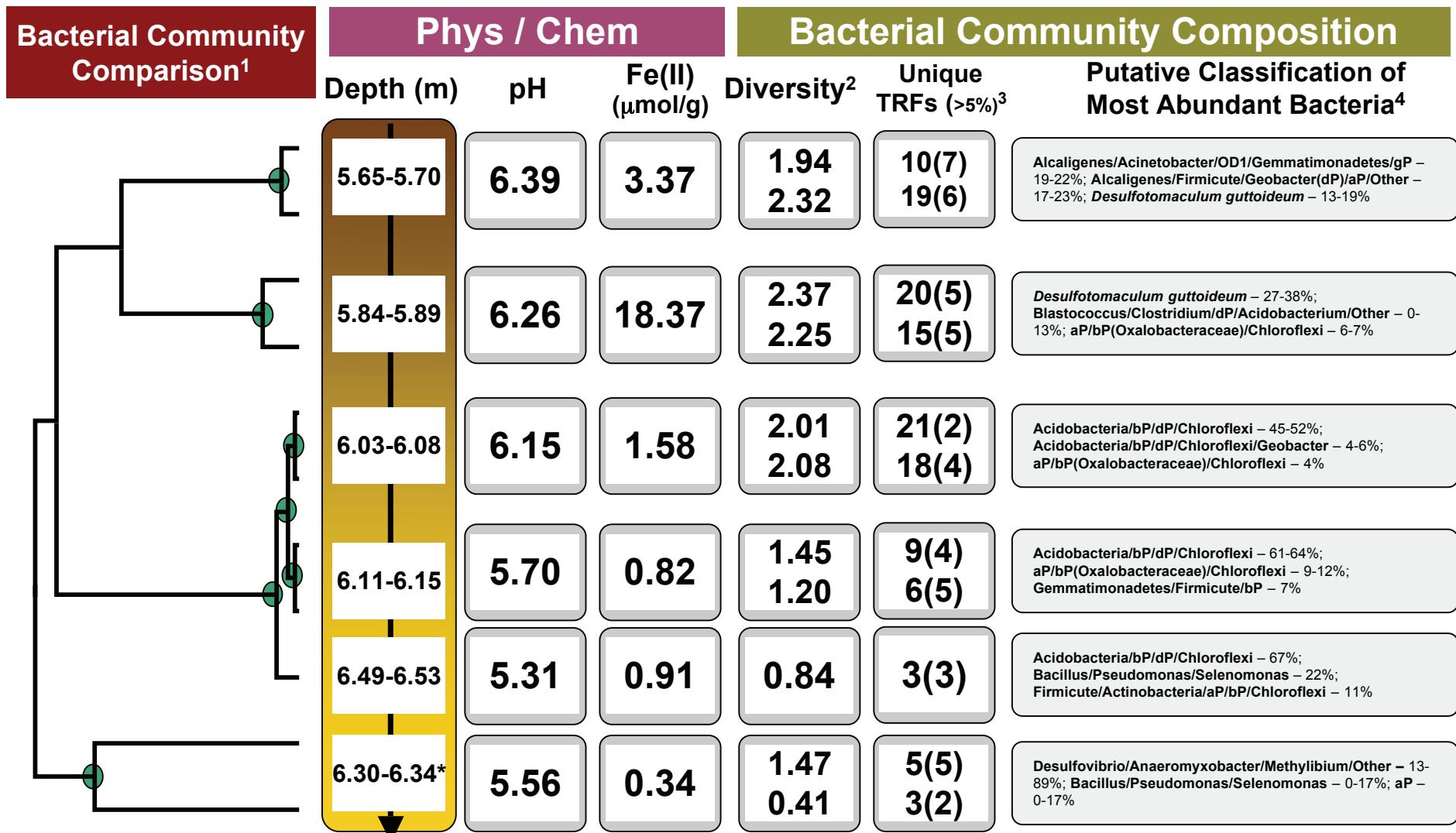
Local Scale Investigations

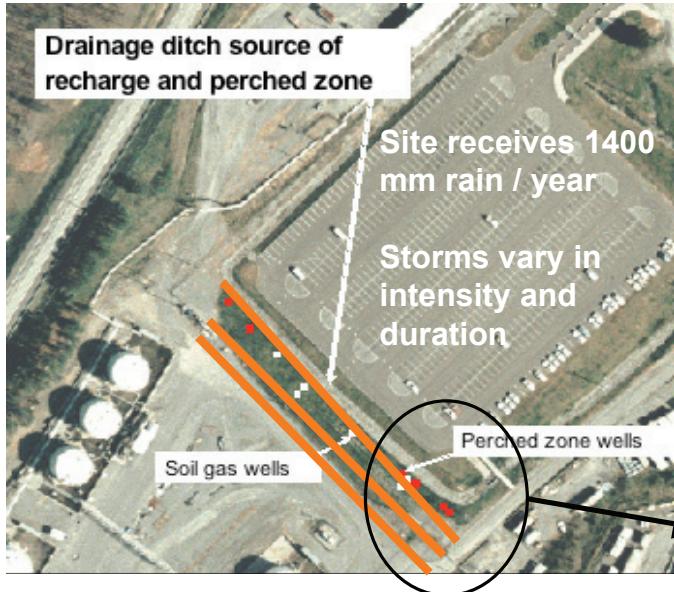
- Experimental design and sampling of material for comparison of groundwater vs. sediment (planktonic vs. attached) populations
- Microcosm denitrification kinetics using $^{15}\text{NO}_3^-$ and ORIFC soil (multiple isotopic abundance approach)





Bacterial Community Composition Analysis of Oak Ridge Area 2 Sediment Samples

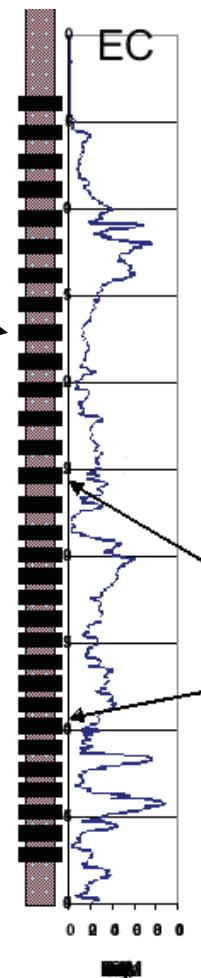




Monitoring perched water table dynamics and interaction with GW as a function of storm events coupled with real time geophysics

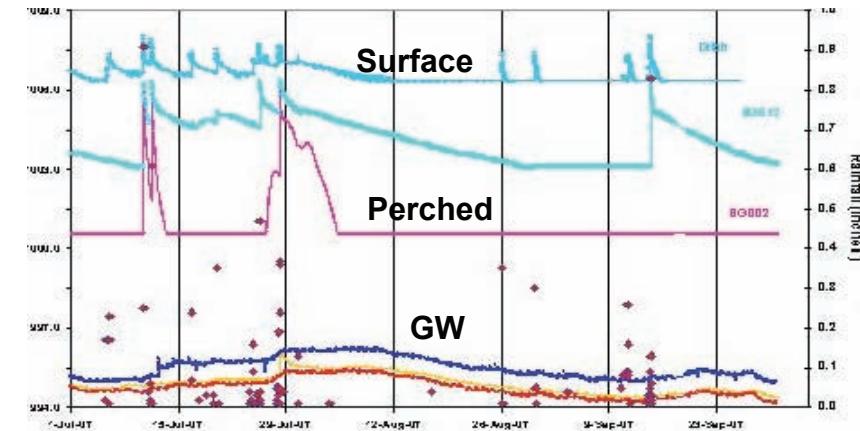
Use of temperature profiles to quantify recharge

Long-term temporal / spatial resolution of recharge impact on contaminant dilution and plumes



Monitoring Natural Recharge

Coupling of traditional hydro-geo-micro measurements with novel real-time geophysics





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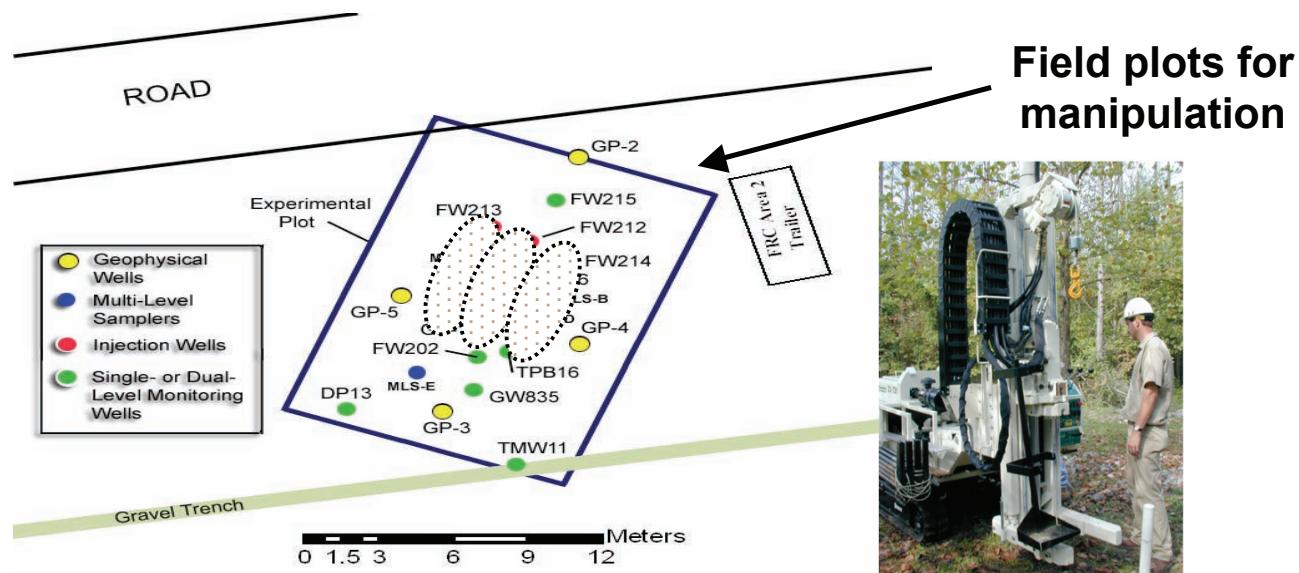


Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate)

Targeted manipulation experiments:

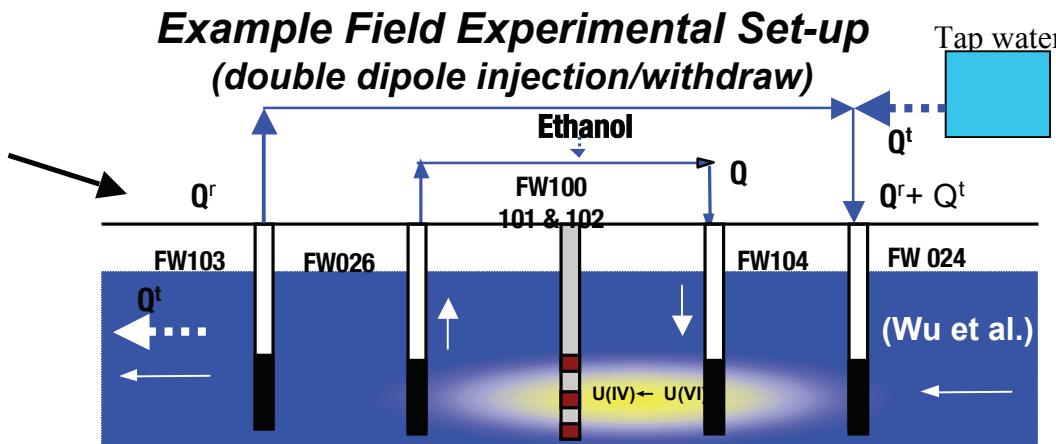
- (1) sustained bioreduction
- (2) pH adjustment
- (3) organo-phosphate amendments
- (4) slow release oleate amendments

Monitor multi-scale hydro-bio-geochemical and geophysical changes and propensity for contaminant remobilization

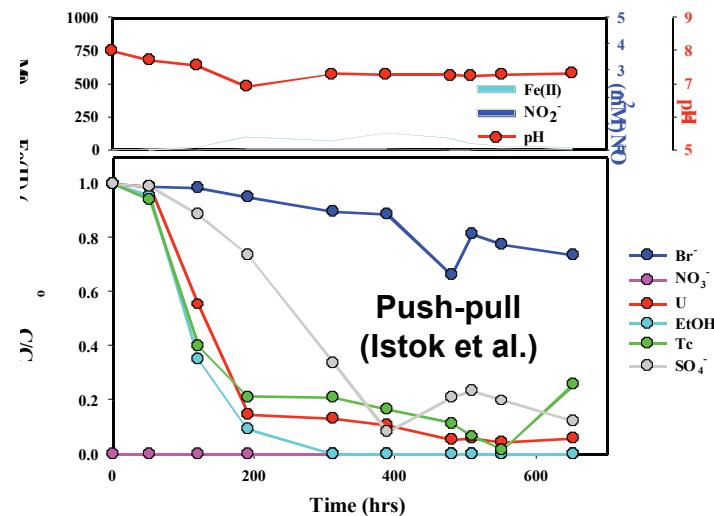
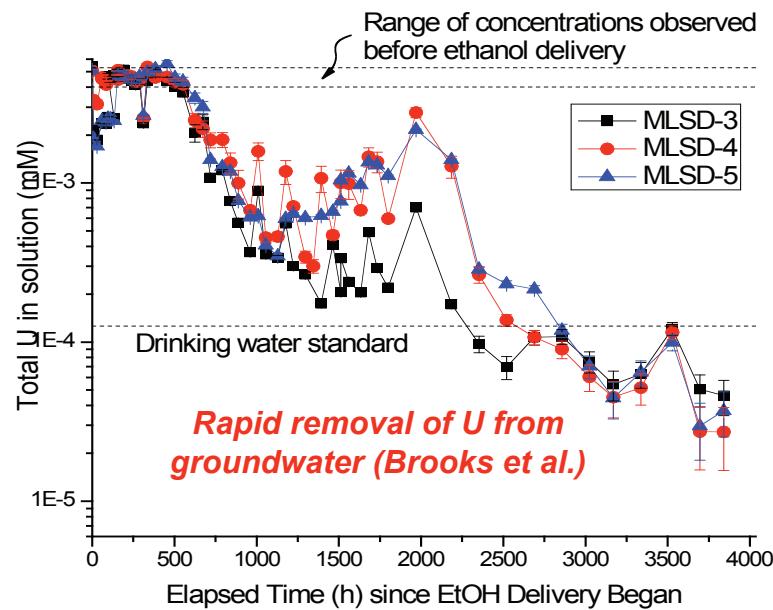




Reduction of mobile U(VI) to sparingly soluble U(IV) via biostimulation following pulsed ethanol (electron donor) injections



**Reduced U(IV)
species sequestered
and immobilized**



**Microbially mediated reduction of U, Tc-99,
and nitrate observed**



OAK RIDGE
INTEGRATED FIELD
RESEARCH CHALLENGE

Targeted Immobilization

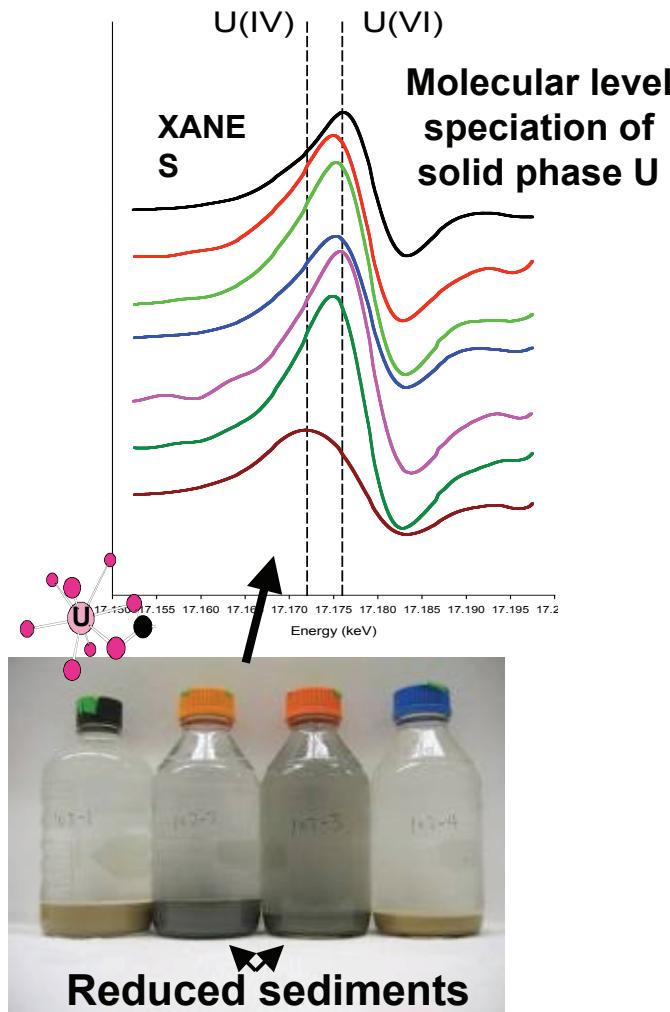
Sustained *in situ* U bioreduction

Microscopic observations



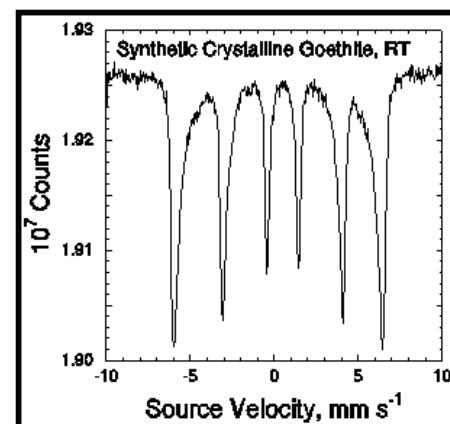
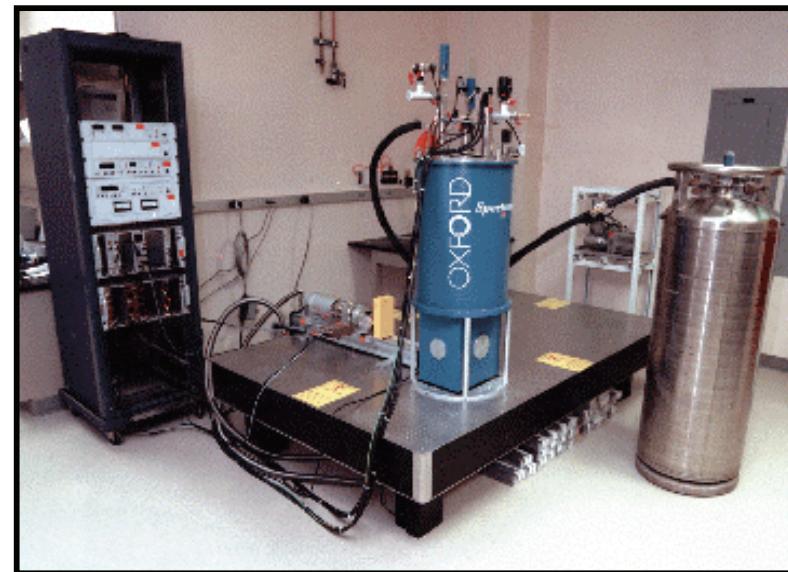
In situ sediments from biostimulated zone show increase in U(IV) due to bioreduction

X-ray Absorption Spectroscopy



Characterizing the role of biogenic Fe(II) on contaminant bioreduction

Mossbauer Spectroscopy



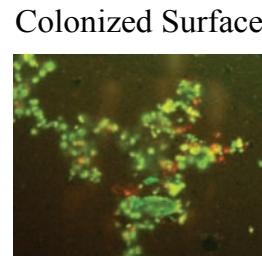
Fe mineralogy before and after biostimulation

Redox buffers to enhance sustainability of contaminant reduction



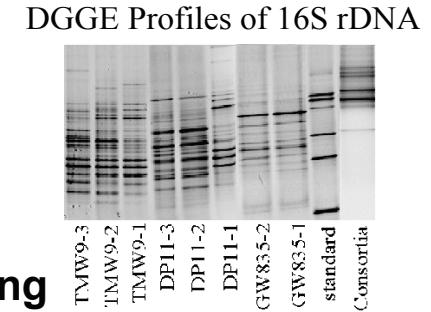
Microbial Community Analysis

Monitored changes / shifts in *microbial communities, activity, abundance, and diversity of organisms involved in nitrate and metal U reduction (SRB, FeRB, NRB)*



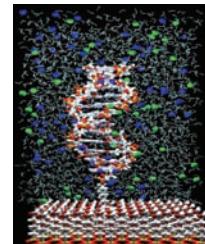
Quantification of microbial activity in groundwater/ sediments during biostimulation tests in parallel with quantification of the change in the abundance/ diversity of sedimentary microbial communities using various cultivation-independent methods

Quantitative MPN (most probable number)-PCR
Cloning and sequencing of 16S rRNA genes



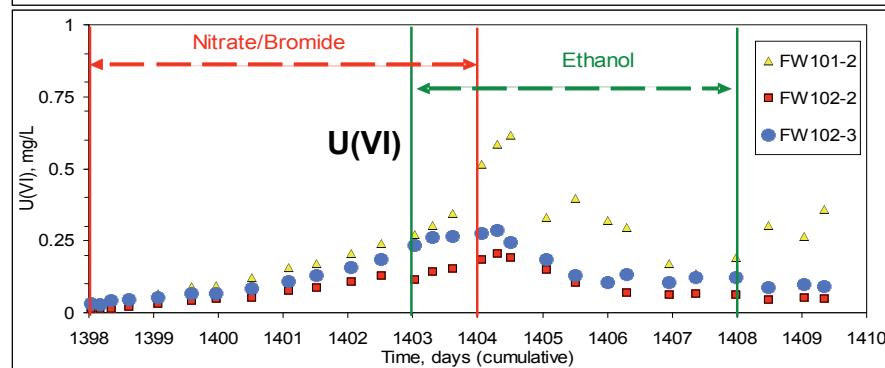
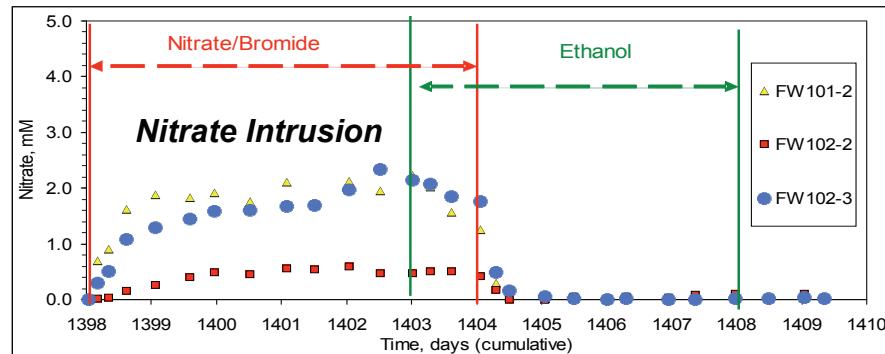
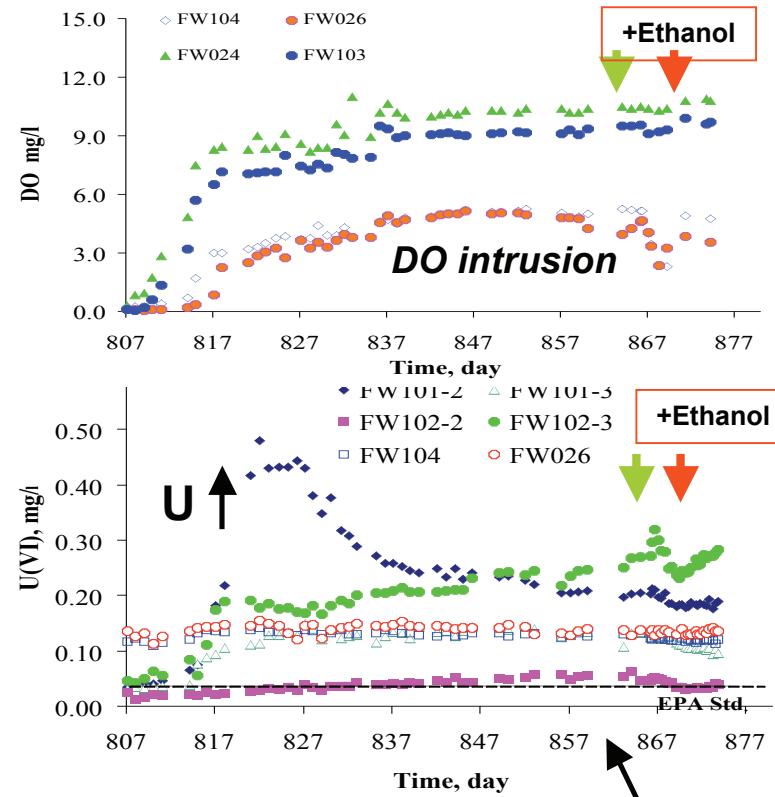
Microbial Array Technologies

Strong relationship between uranium concentrations and the total abundance of c-type cytochrome genes and *dsrAB* genes in bio-stimulated zone using array technologies





Intrusion of DO and nitrate on U(IV) reoxidation



Kinetics of U(IV) reoxidation rapid in the presence of significant groundwater DO suggesting anaerobic conditions are necessary for *in situ* U immobilization. (*Thiobacillus* was present in the sediments and also detected in groundwater after DO reoxidation. This microorganism may play a role in oxidation of FeS and U(IV)).

Kinetics of U(IV) reoxidation rapid in the presence of co-contaminant nitrate, the latter being easily removed via denitrification assuming concentrations are reasonable (ppm levels vs. pp-thousand). (Geobacter may also play a role in the oxidation of U(IV) to U(VI) in the presence of nitrate).



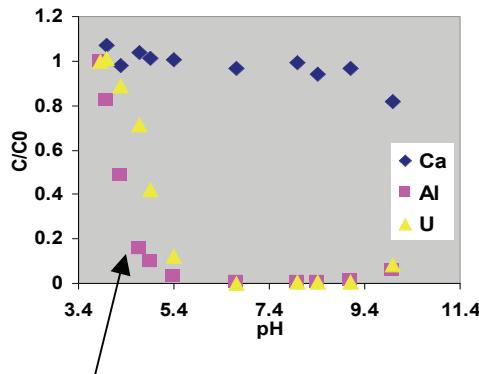
- Investigate strategies for *slowly* adjusting groundwater pH to effectively immobilize U(VI) and Tc through sorption and/or co-precipitation with Al-oxyhydroxides

mechanism of Al precipitation and U co-precipitation highly dependent on rate and concentration of base addition

ORIFC has high dissolved Al concentrations in groundwater near source (e.g. > 500 ppm)

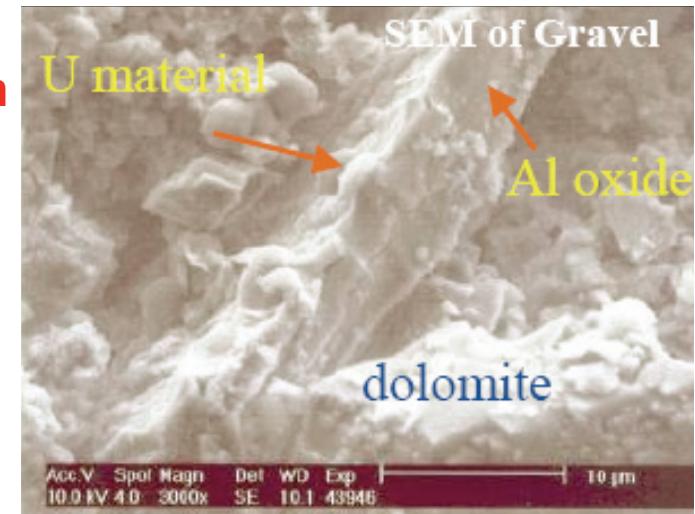
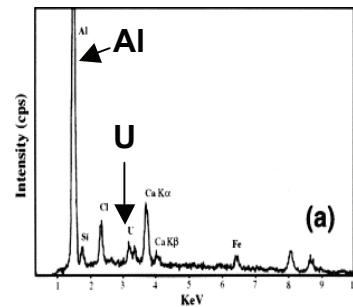
- Investigate controlled additions of silicate [as $\text{Si}(\text{OH})_4$] and hydroxide to induce the formation of sparingly soluble aluminosilicates and thus an increased stability of immobilized U(VI)
- Investigate the influence of increased pH towards enhancing subsurface microbial activity, community diversity and rates of denitrification downgradient of a field-scale pH-manipulation zone

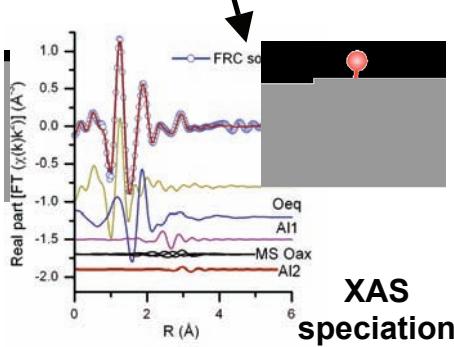
ORIFC Groundwater near source



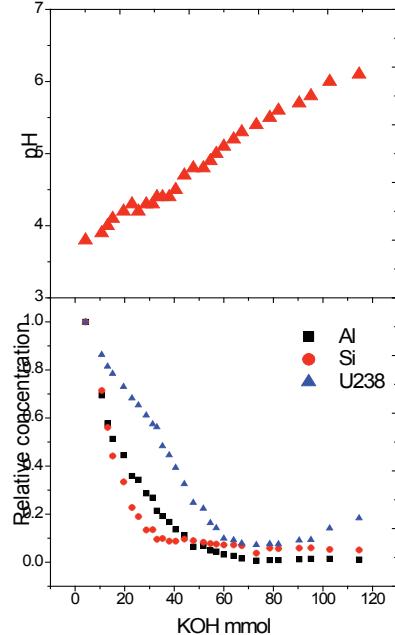
Aluminum precipitates from solution with increase in pH and a loss of U that follows

Strong correlation between U and Al at the IFC





pH and effluent concentrations
of U and other metal ions



Targeted Immobilization Immobilization via pH manipulation

Intermediate Flow Experiments

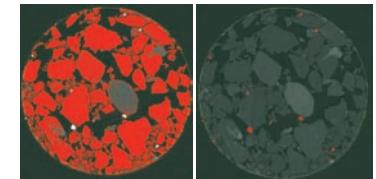
Column flow experiments determine optimal parameters for *in situ* conditions (e.g. concentrations, flow rates and interruptions, hydraulics, mass balances). Complement batch titration experiments

Geochemical, mineralogical, and microbiological characterization before and after manipulation

Needed for geophysical calibration and modeling during scale-up to field

Microtomographic imaging

being performed at LBNL Advanced Light Source to explore changes in matrix structure and geophysical attributes associated with evolved precipitates at ~the scale of the process



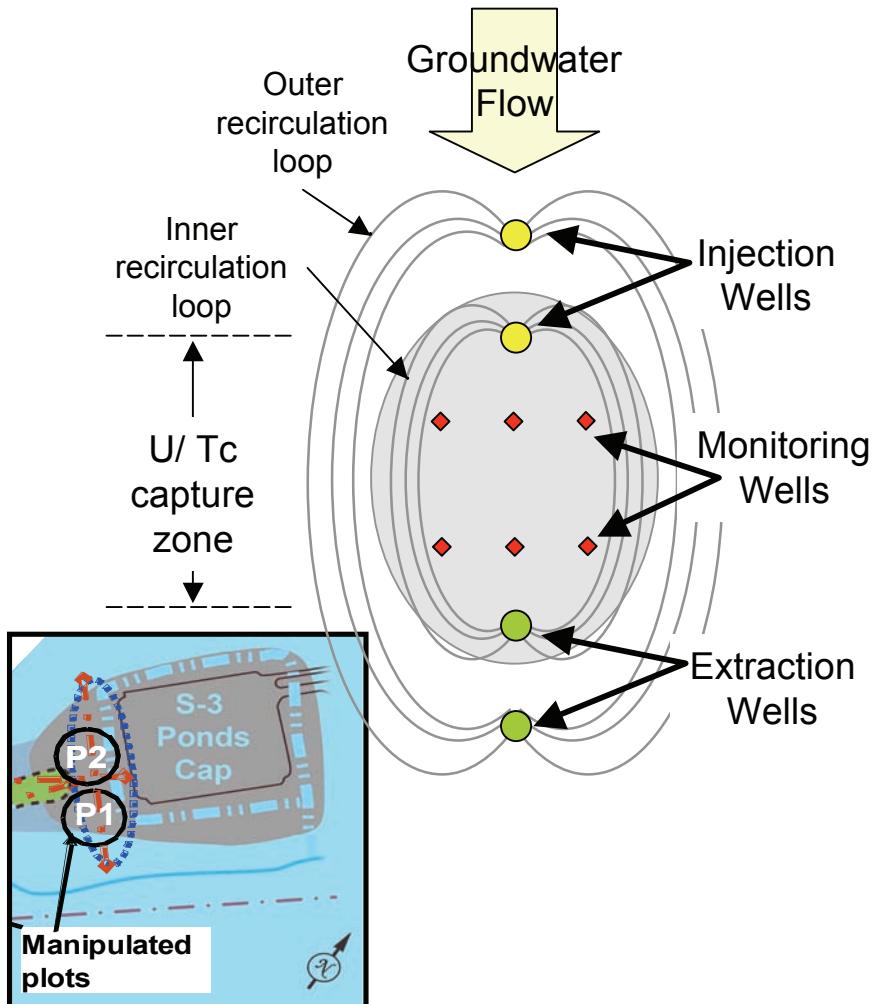
Lab equipment set up to enable development of biogeochemical-geophysical petrophysical relationships (with particular attention to development of precipitates and seismic imaging)





Near-term field experiment (source control)

Double dipole injection/withdraw strategy



- Laboratory columns showed that co-precipitated uranyl appears to bind to aluminate in sediments and is less exchangeable or extractable than those sorbed uranyl.
- Field plot set up and characterization underway (e.g., multi-tracers studies, geophysical, mineralogical, and microbiological analysis - baseline).
- Long-term, controlled pH adjustment - field injection experiment

Monitoring the precipitation or coprecipitation of U/Tc and the formation and transport of Al-oxyhydroxides for creating a subsurface capture zone for U(VI)/Tc(VII) immobilization

Coupled tracer studies, geophysical, microbiological, mineralogical, and speciation studies.



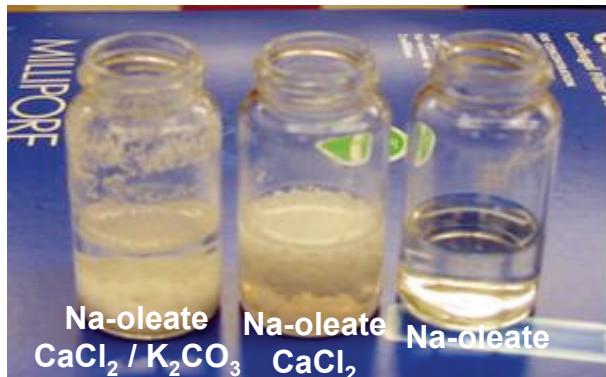
Targeted Immobilization
Slow release electron donor

Ca-oleate

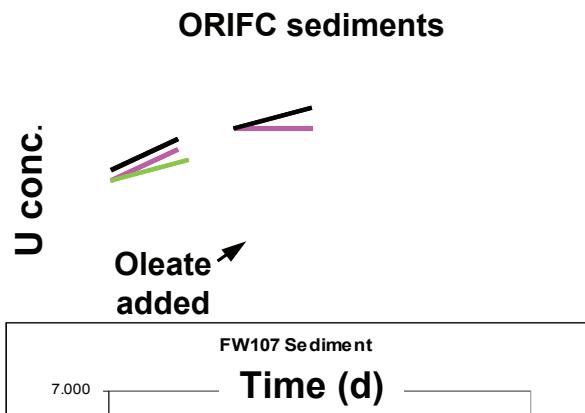


Use of Ca-oleate as a slow release electron donor source for subsurface microbial stimulation and bioreduction of U(VI) to sparingly soluble U(IV)

Investigations on the rates and mechanisms of the oleate precipitation reaction, the mode of subsurface delivery, and the specific microorganisms that are stimulated and knowledge of what their specific activity is with regard to U(VI) reduction

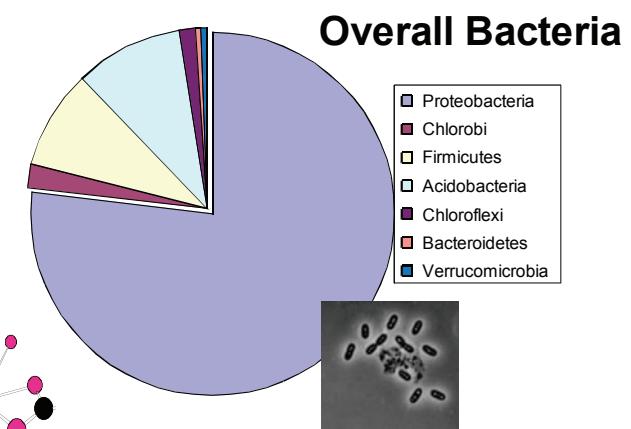


The microcosm test is a feasibility screen test to verify the presence of oleate degraders and propensity for U(VI) reduction.



Desulforegula and Geobacter spp. may be involved in oleate degradation

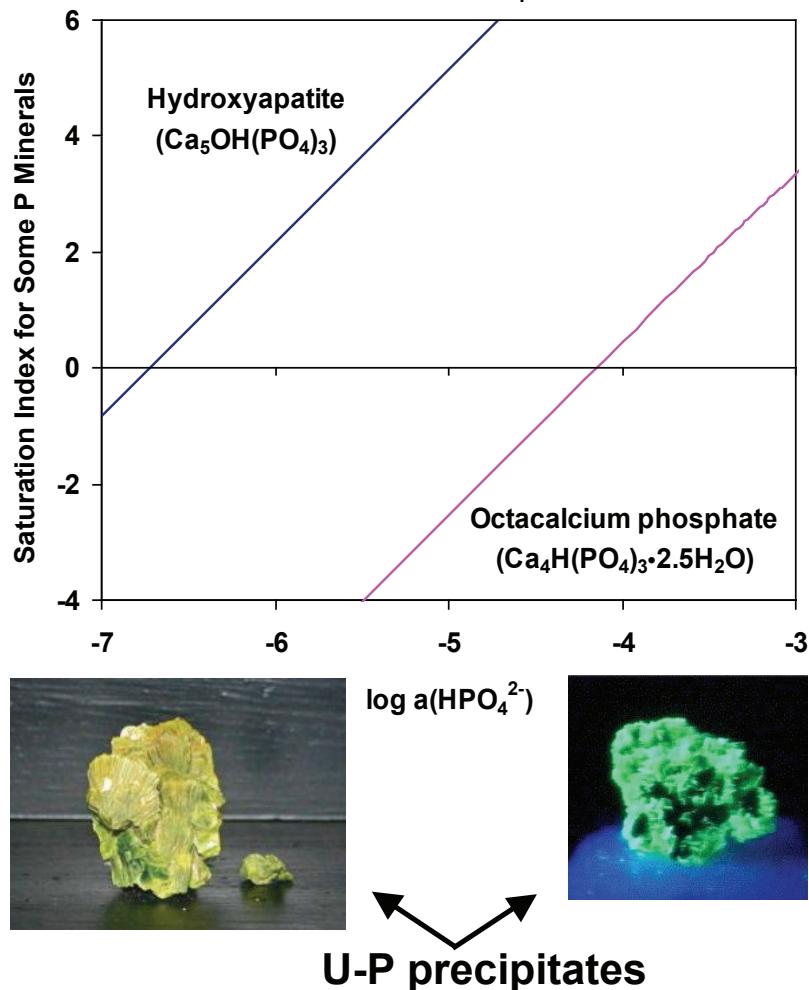
XANES confirmed formation of U(IV)





Taking advantage of low U-P solubility

Saturation index for some phosphate minerals in representative ORIFC groundwater as a function of the logarithm of HPO_4^{2-} activity.



The immobilization of U via the formation of low solubility U-bearing phosphate minerals is a naturally occurring process

A major limitation to the use of inorganic phosphate (IP) as a groundwater amendment is the low mobility of IP in subsurface environments (highly reactive with mineral oxides and clay minerals)

Using organo-phosphate may overcome this limitation by:

(1) allowing for the enhanced migration of the P source

(2) the reliance on microorganisms to liberate enough free IP, during OP transport, to promote the precipitation of poorly soluble phosphate - U minerals

or

(3) phytic acid, hydrolysis half-life ~100y for Ca precipitate, U selectivity much greater than Ca



Presentation Outline

- ORIFC Objectives / Goals / Site Description
- ORIFC Approach (Tasks A – D)
- Year-1 Results and Future Research

Watershed Characterization: Define flowpaths and heterogeneities that control the fate and transport of contaminant plumes

Quantifying Natural Attenuation Processes: Define and quantify natural attenuation rates & mechanisms for U, Tc, and co-contaminant NO₃ across the Bear Creek watershed

Targeted Immobilization Strategies: Quantitative *in situ* immobilization strategies within secondary sources of the saprolite and carbonate units (U, Tc, nitrate) using coupled geochemical and microbial techniques

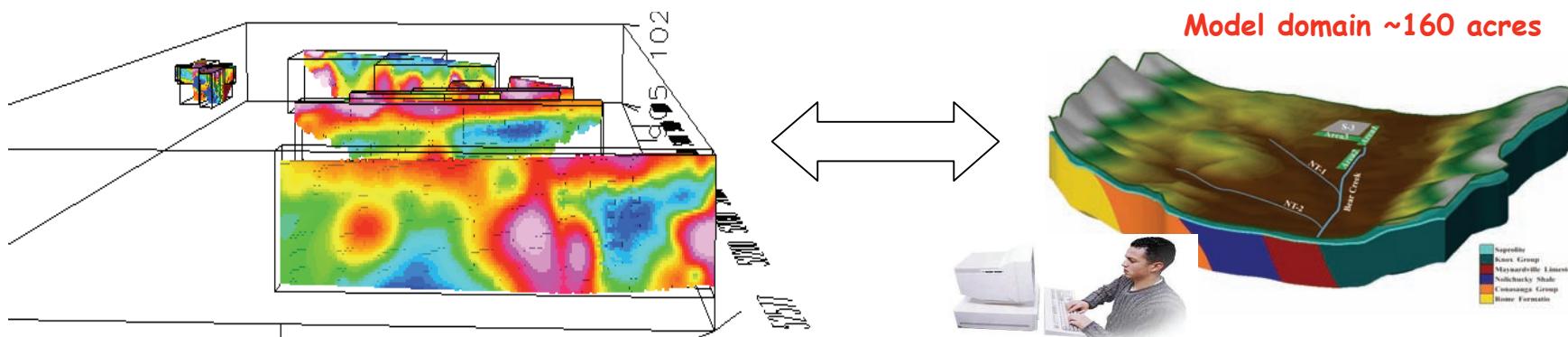
→ ***Multi-scale, Multi-process Modeling:*** Numerical modeling and data analysis from the molecular to the watershed scale

- Information Sources / Technology Transfer / Opportunities



Multiprocess and Multiscale Numerical Modeling and Data Analysis

- Model Implementations as a function of scale: HydroGeoChem used to analyze lab, field plot, and watershed wide datasets at the Oak Ridge IFC site.
- Modeling multi-scale laboratory datasets of U and Tc Immobilization through pH Adjustment
 - GW titration modeling
 - Soil pH buffer modeling
 - Soil titration modeling
 - pH manipulation column modeling
- Investigations of various numerical methods to solve transport problems
- GW heat transfer model for estimating GW recharge and surface water discharge associated with precipitation events





Modeling Approach

HydroGeoChem (HGC) v.5 serves as the primary modeling tool
(multi-process multi-component flow and transport code)

Capabilities:

- Three-dimensional domain with any spatial structure
- Transient sat/unsat flow in heterogeneous, fully anisotropic media
- Multi-species aqueous phase transport coupled with flow to include density-dependent effect
- Adaptable to model reaction-flow coupling (e.g., pore clogging)
- Generic application of biogeochemical reaction network (equilibrium and kinetic)
- Diffusion-limited mass transfer kinetics
- Coupled with nonlinear inversion code PEST to perform parameter estimation
- Readily applicable to any DOE site





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Multi-scale, Multi-process Modeling

Batch and intermediate scale model simulations

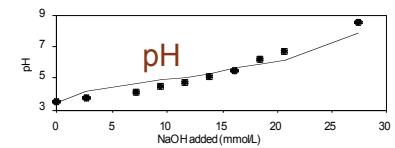


Modeling multi-scale laboratory datasets of U and Tc Immobilization through pH Adjustment

- GW titration modeling
- Soil pH buffer modeling
- Soil titration modeling
- pH manipulation column modeling



Precipitation/dissolution Reactions	logK
$\text{Al(OH)}_{3,\text{microcrystalline}} + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	9.35
$\text{MnCO}_{3,\text{synthetic}} = \text{Mn}^{2+} + \text{CO}_3^{2-}$	-10.39
$\text{FeCo}_{0.1}(\text{OH})_{3.2} + 3.2\text{H}^+ = \text{Fe}^{3+} + 0.1\text{Co}^{2+} + 3.2\text{H}_2\text{O}$	5.7
$\text{Ni(OH)}_2 + 2\text{H}^+ = \text{Ni}^{2+} + 2\text{H}_2\text{O}$	10.8
$\text{CaUO}_4 + 4\text{H}^+ = \text{Ca}^{2+} + \text{UO}_2^{2+} + 2\text{H}_2\text{O}$	15.931
$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O} + 6\text{H}^+ = \text{Ca}^{2+} + 2\text{UO}_2^{2+} + 2\text{Si}(\text{OH})_4^0 + 5\text{H}_2\text{O}$	9.42
Soil Buffering Reactions	LogK
$\text{H}_4\text{X} = \text{H}_3\text{X}^- + \text{H}^+$	-3
$\text{H}_3\text{X}^- = \text{H}_2\text{X}^{2-} + \text{H}^+$	-6
$\text{H}_2\text{X}^{2-} = \text{HX}^{3-} + \text{H}^+$	-9
$\text{HX}^{3-} = \text{X}^{4-} + \text{H}^+$	-11
Ion-exchange Reactions	logK
$\text{Y}_2\text{SO}_4 + \text{UO}_2(\text{CO}_3)_2^{2-} = \text{Y}_2\text{UO}_2(\text{CO}_3)_2 + \text{SO}_4^{2-}$	4.04 ± 1.36
$2\text{Na}^+ + \text{CaX}_2 = 2\text{NaX} + \text{Ca}^{2+}$	-0.884 ± 0.310
$2\text{Na}^+ + \text{MgX}_2 = 2\text{NaX} + \text{Mg}^{2+}$	-0.884 ± 0.310
$2\text{Na}^+ + \text{SrX}_2 = 2\text{NaX} + \text{Sr}^{2+}$	-0.884 ± 0.310
$\text{Mn}^{2+} + \text{CaX}_2 = \text{MnX}_2 + \text{Ca}^{2+}$	0.578 ± 0.126
$\text{Ni}^{2+} + \text{CaX}_2 = \text{NiX}_2 + \text{Ca}^{2+}$	0.578 ± 0.126
$\text{Co}^{2+} + \text{CaX}_2 = \text{CoX}_2 + \text{Ca}^{2+}$	0.578 ± 0.126
$\text{UO}_2^{2+} + \text{CaX}_2 = \text{UO}_2\text{X}_2 + \text{Ca}^{2+}$	1.32 ± 0.12



SO₄

Al

U

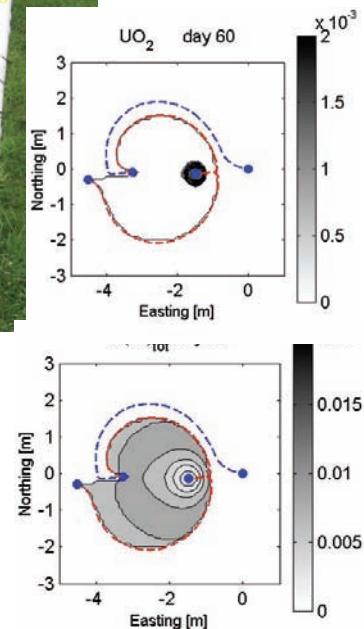
Mg Ca
Sr

Ni Mn
Co

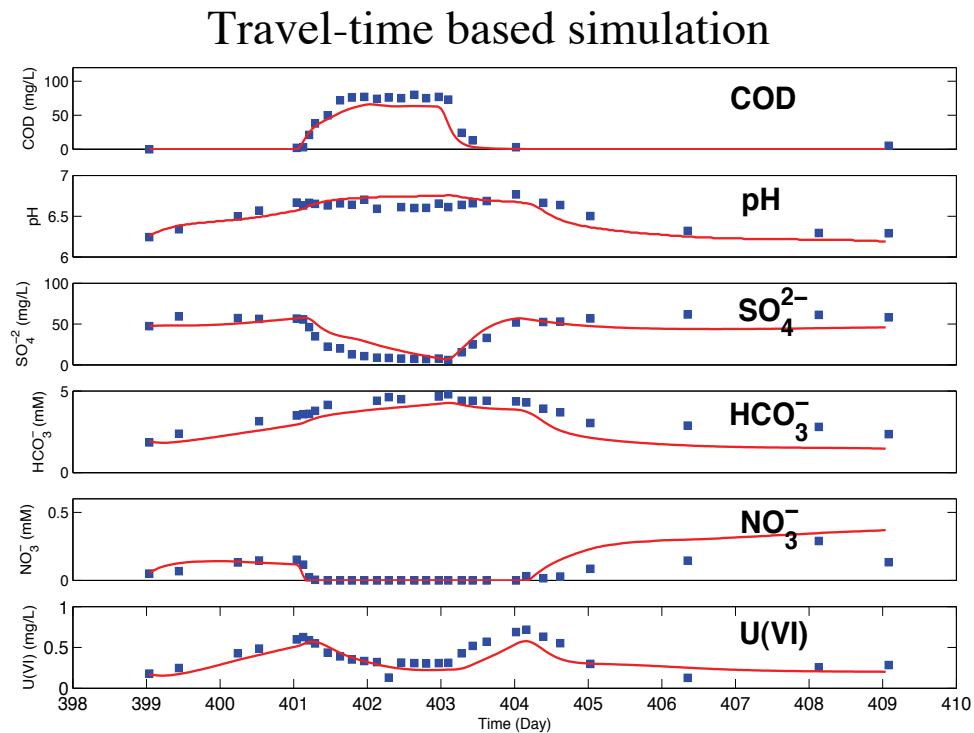


Field plot modeling of U(VI) bioreduction

A travel-time based reactive transport model was developed to simulate the *in situ* bioreduction field plot experiment for demonstrating enhanced bioreduction of U(VI)



Travel-time based visualization

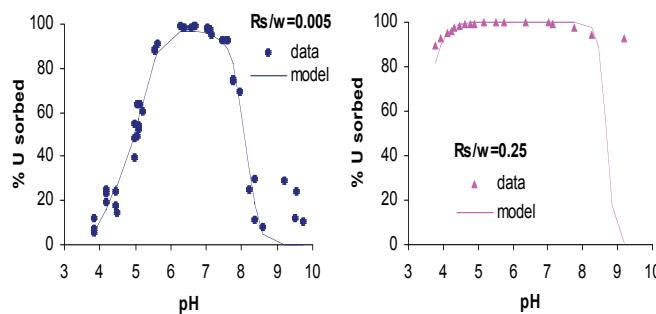


Model considers microbial reduction of nitrate, sulfate, and U(VI)

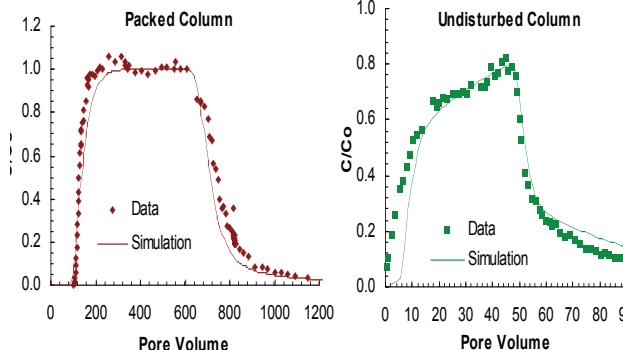


Model Implementations: HydroGeoChem has been used to analyze laboratory, plot, and watershed scale data on the Oak Ridge IFC site

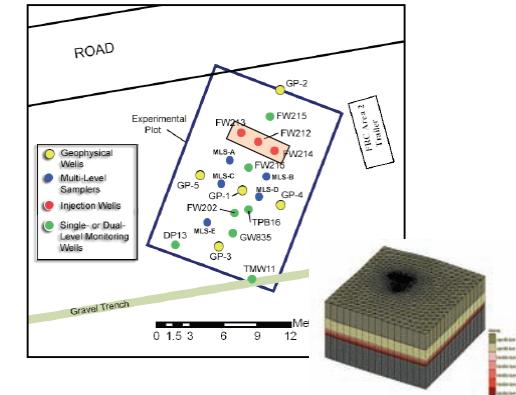
Batch U-Sorption Experiments



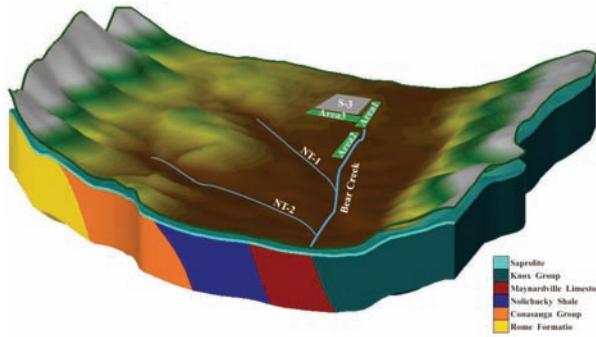
Lab U-Column Experiments



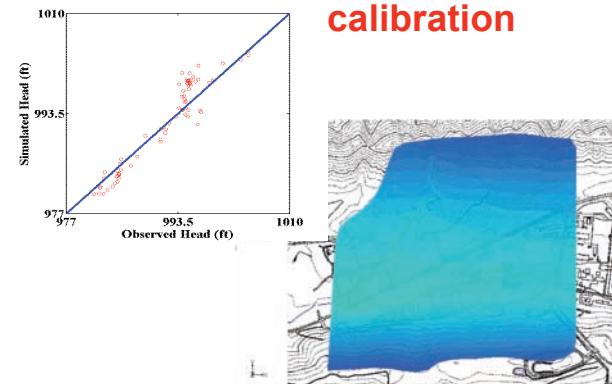
Field Scale Manipulations



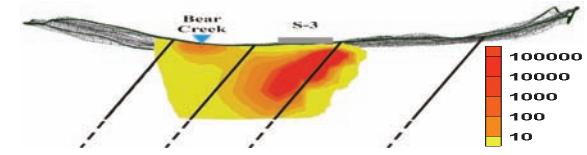
Model domain ~160 acres



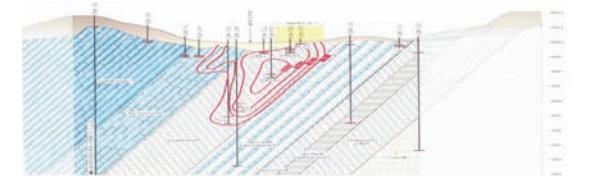
Groundwater calibration



Simulated NO₃⁻ plume with density-dependent flow



Observed plume



Calibrated model used to simulate large scale nitrate transport



Research Outcomes & Site Contributions

Multi-scale predictive monitoring and modeling tools that can be used at sites throughout the DOE complex to inform and improve the technical basis for decision making, and to assess which sites are amenable to natural attenuation and which would benefit from source zone remedial intervention.

Recommendations and strategies, conveyed via technical reports and stakeholder workshops, that will assist local decision makers with scientifically informed choices on ground water remediation actions relevant to ORR EM groundwater problems between 2012 -2015.

Integration of research findings and lessons learned across all ERSD IFC sites through the sharing of knowledge regarding the influence of coupled processes on natural and engineered processes in contaminated subsurface environments.

Scientific publications that convey our improved multi-scale conceptual and predictive understanding of manipulated and natural contaminant attenuation rates and mechanisms and the long-term effectiveness of remedial activities relevant to *in situ* remediation and stewardship at DOE sites.





Data Management

Characterization and other data of wide appeal are being loaded into a central database

- Data is searchable and accessible via a Web interface.
- Map-based queries are available.

Data resulting from investigator experiments will be documented using a Web-based metadata entry tool

- Controlled vocabulary and indexing terms will ensure consistency in the data descriptions.
- The metadata will contain hyperlinks to the associated data.
 - Initially the metadata and associated data will have access limited to project personnel.
 - However, all data and documentation will eventually be searchable and accessible by anyone from the ORFRC website.
- Each investigator will create their own data sets in consultation with IFRC-ORFRC data manager.
- All data will be stored on ORNL file server.



A publicly accessible **ORIFC website** (<http://www.esd.ornl.gov/orifrc/>) is available for the distribution of information and data to the broader scientific community, EM, regulators and the public. Project characterization data and research findings are periodically transferred to the Oak Ridge Environmental Information System for use by environmental decision makers.

Over 35 new and 70 previous peer-reviewed publications (>100 total) have resulted from the new IFC project and past ORFRC site characterization and research, respectively. Site-wide conceptual and numerical models have been developed and continue to be improved. ORIFC groundwater and sediment samples have been sent to 15 independent ERSD researchers this past year.

The project PI and Field Research Manager have been active participants in the DOE Oak Ridge Reservation Closure Project Team in order to ensure remediation planning needs are addressed and technical insights are transferred into DOE remediation efforts





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Backup Slides



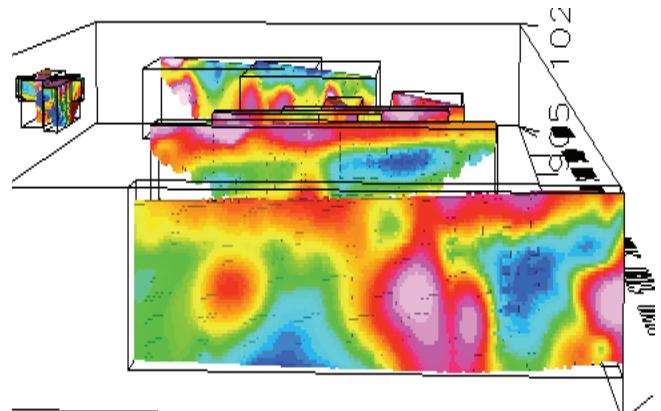
OAK RIDGE
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Summary



Watershed Scale Characterization

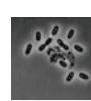
Contaminant pathways and media properties using surface geophysics



Cross-correlation with traditional macroscopic measurements (e.g conductivity profiles, refusal, and water quality data)

Targeted Immobilization

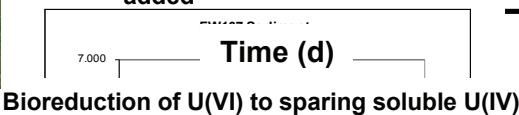
Bioreduction, pH adjustment, slow release electron donor (oleate), organo-phosphate



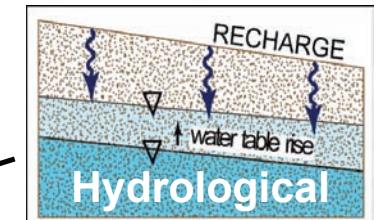
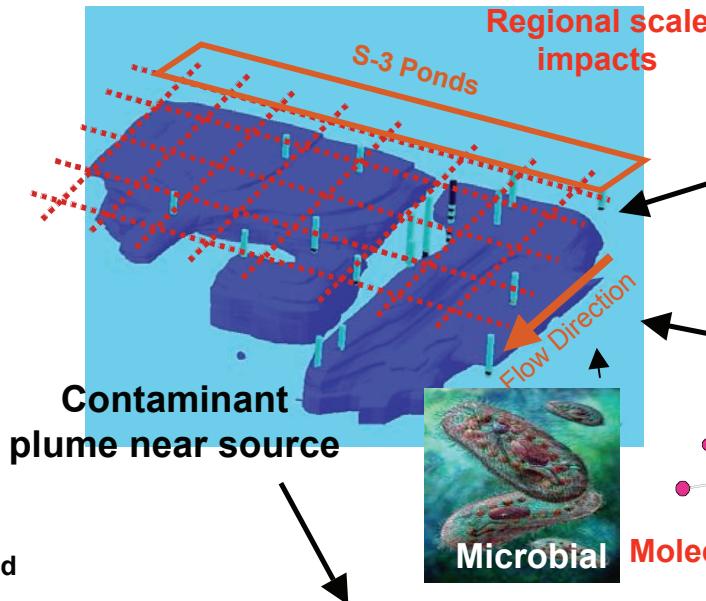
ORIFC sediments

U conc.

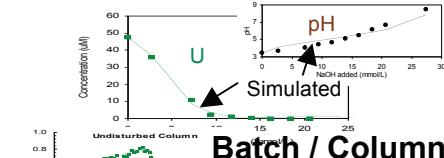
Oleate added



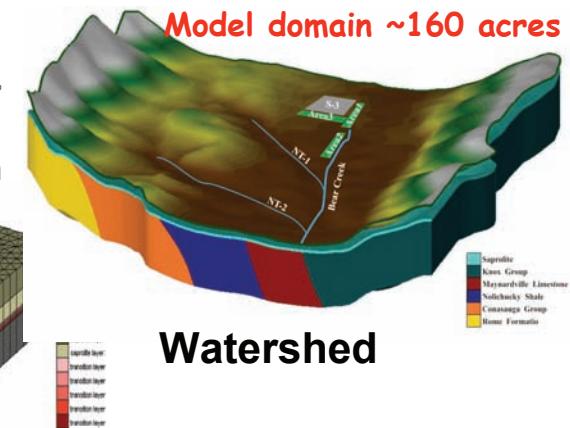
Natural Contaminant Attenuation



Multiscale, Multiprocess Modeling (enhanced predictive capability)



Field plot





Relevance

This project is intimately connected with the [ORR Groundwater Strategy Document](#) (DOE 2004) which emphasizes the need for timely and focused research investigations on natural hydrogeologic systems at the ORR to help evaluate the technical feasibility and cost-effectiveness of various remediation strategies including natural attenuation.

The results of our proposed research will have maximum impact on ORR groundwater remediation decisions since groundwater decisions are slated for 2012 – 2015, which is the same time period that our project ends.

We will provide an enhanced scientific understanding of subsurface processes through improved multi-scale characterization and numerical modeling tools that are needed to predict contaminant fate and transport under a variety of remediation scenarios.

David Watson is an invited member of the [ORR Groundwater Core Team](#) that seeks to “facilitate the identification, funding, and implementation of high-priority science and technology investigations” as related to ORR site groundwater issues.

This team works with state regulators, remediation contractors, and the DOE ORR Closure Project Core Teams to focus efforts on *the goal of site closure*.

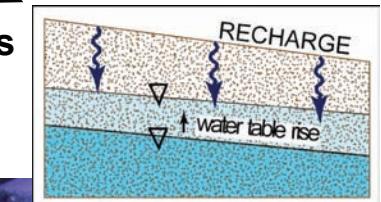
Characterization data and research findings from the ORFRC will continue to be input into the [Oak Ridge Environmental Information System \(OREIS\)](#), which is the long-term repository for data generated by the ORR EM and compliance programs for use in decision making.



Objectives

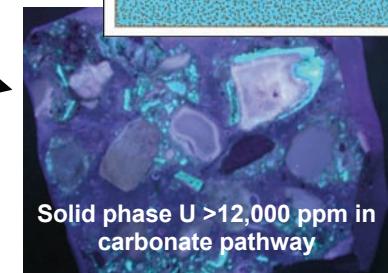
(1) quantify spatial and temporal aspect of transient recharge and other hydraulic drivers for groundwater flow and dilution

- episodic events, seasonally, and long term along contaminant pathways



(2) determine the rates and mechanisms of coupled hydrological, geochemical, and microbiological processes that control the natural attenuation of contaminants

- highly diverse subsurface environments over scales ranging from molecular to watersheds



(3) explore novel strategies for enhancing the subsurface stability of immobilized metals and radionuclides.

- strategic manipulations of hydrology, geochemistry, microbiology



(4) understand the long-term impacts of geochemical and hydrological heterogeneity on the remobilization of immobilized radionuclides.

- redox, pH, complexation, sorption, recharge, preferential flow, diffusi

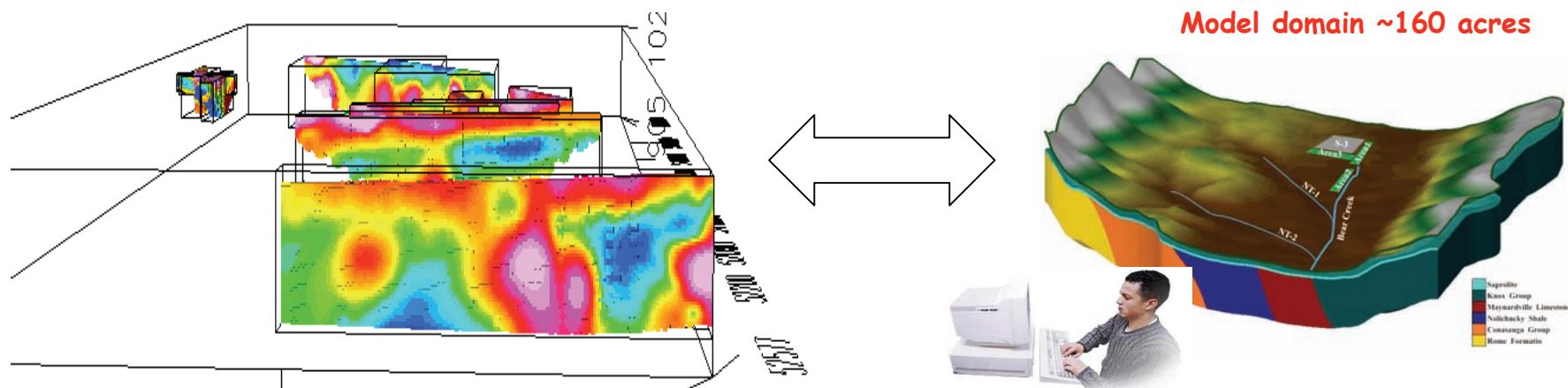


(5) improve our ability to predict the long-term effectiveness of subsurface remedial activities and natural attenuation processes

- subsurface contaminant behavior across a variety of scales.



- Continue to advance methods that permit quantitative use of geophysical datasets for watershed characterization and monitoring (i.e. delineate watershed-scale subsurface heterogeneities and contaminant pathways)
- Provide insights into rates and mechanisms of geochemical and hydrological processes associated with natural episodic, seasonal, and annual recharge over field-relevant scales
- Provide parameterization/validation to local and site wide models



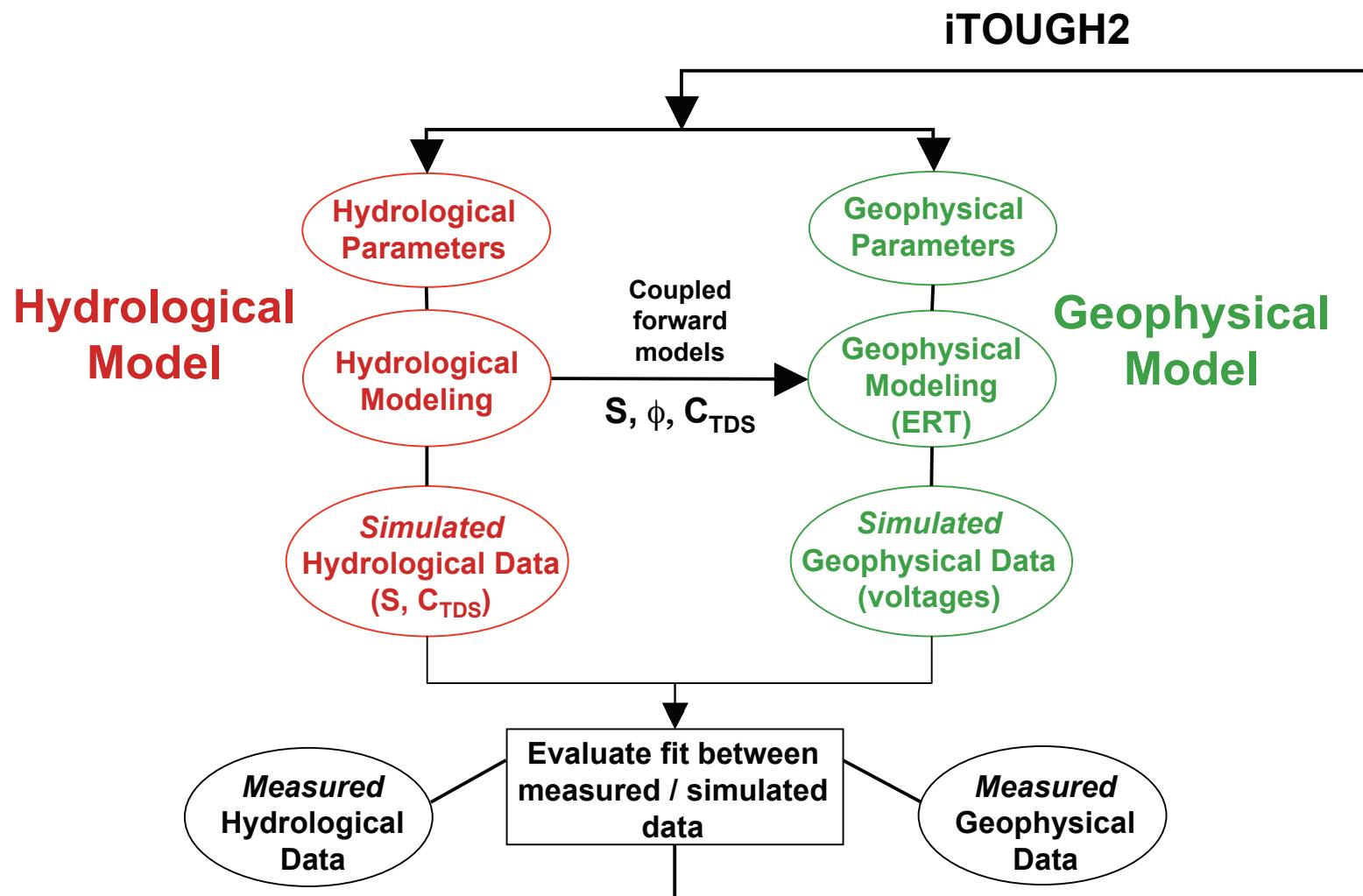


OAK RIDGE

ENVIRONMENTAL
REMEDIAL

RESEARCH CHALLENGE

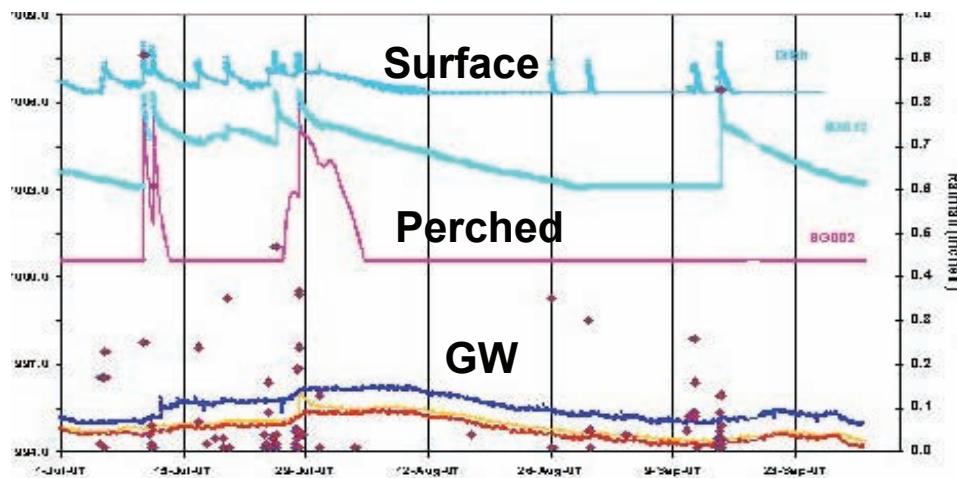
COUPLED MODELING OF HYDROLOGICAL-GEOPHYSICAL DATA SETS



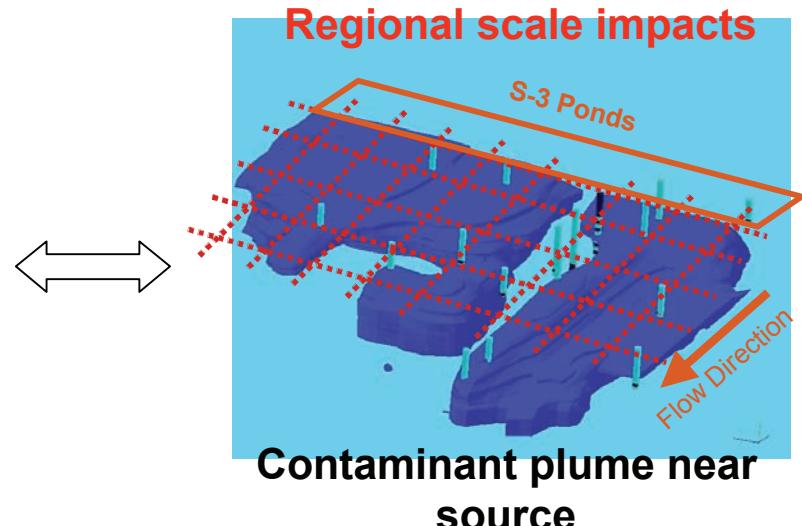


- Continue to collect watershed scale databases that couple contaminant concentration, pH, redox conditions, microbial activity, reactivity, etc. on U, Tc, and nitrate natural attenuation (geophysics, isotopes, spatial and temporal variability along pathways and transition zones).
 - Link with smaller scale observations and couple with site-wide multiprocess, multicomponent numerical model.
- Continue to quantify the impact of recharge on geochemistry, contaminant dilution, O₂, carbon source, microbial activity, etc. on spatial and temporal plume dynamics.
- Coupled hydrobiogeochemical measurements with real-time geophysics for quantifying large scale spatial and temporal changes in contaminant plume dynamics as a function of long-term seasonal patterns and short-term storm events.

Local scale monitoring



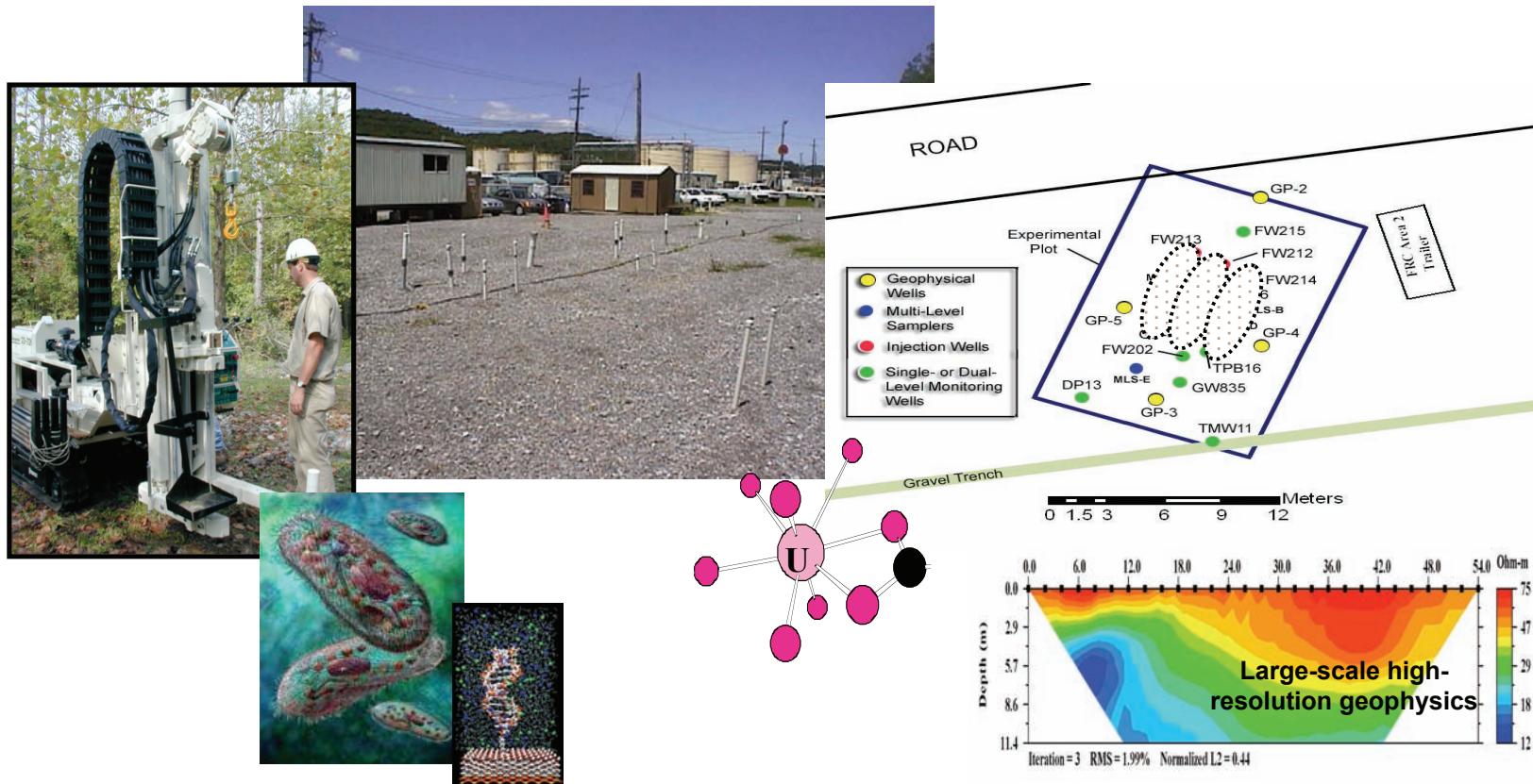
Regional scale impacts





Future Research – Task C

- Targeted U and Tc immobilization through up-scaled pH, oleate, and organo-phosphorous experiments via intermediate and field investigations.
 - Large plot scale pH manipulation, cm-m scale oleate manipulation
- Intensive coupling of hydrology, geochemistry, geophysics, microbiology, and interfacial surface spectroscopy.





U(VI) Reduction by Slow Release Substrate (SRS)



SRS source: Terra Systems, Inc., Wilmington, DE

Composition: vegetable oil (70%), sodium lactate (5%), yeast extract (1%), $(\text{NH}_4)_3\text{PO}_4$ (1%)

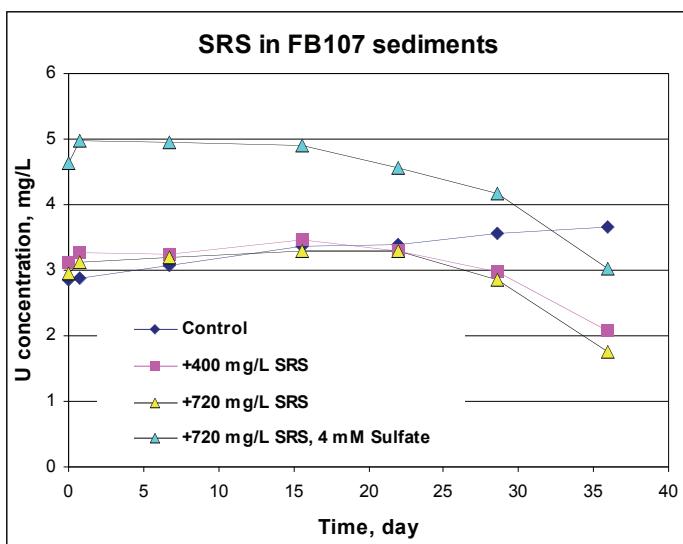
Microcosm Test Conditions

Sediments: FB107, U content: 700 mg/kg

Groundwater: FW231-2

SRS: 720 mg/L as COD

Primary Results: Bioreaction occurred after two weeks. U reduction detected after 4 weeks. The color of the sediments changed. The test is still in progress.



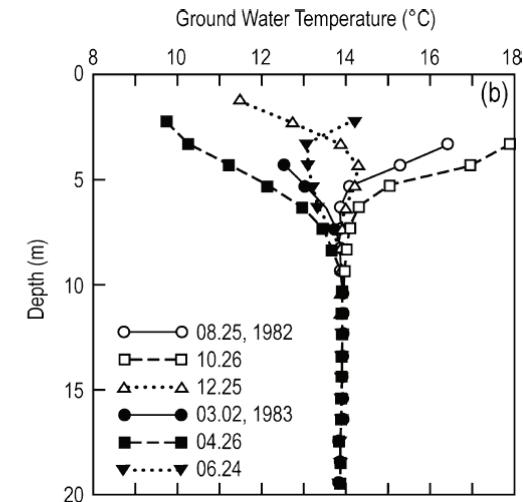
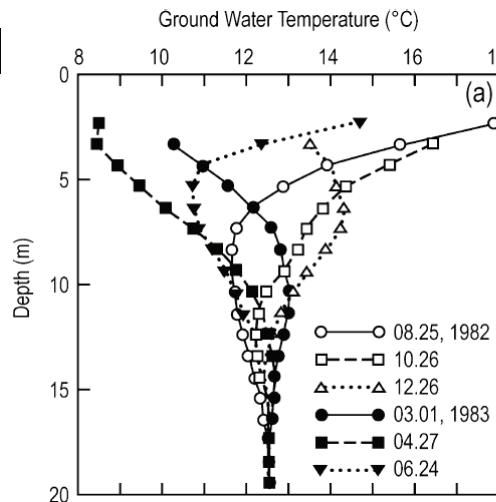


Results – Task D

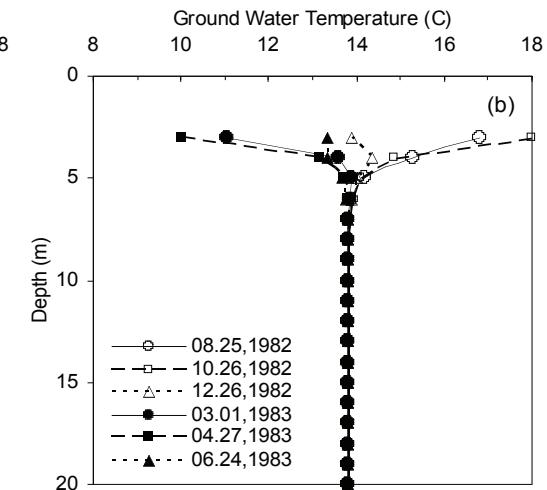
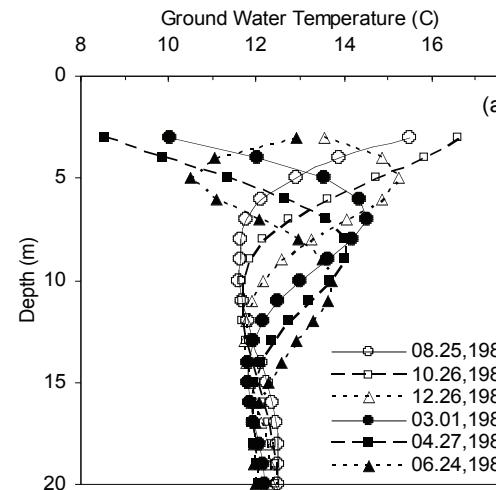
GW heat transfer model

Temperature profiles in the surficial zone potentially provide information about seasonal precipitation events and interchange with surface water

Temperature data can be used in inverse problems to estimate GW recharge and surface water discharge associated with precipitation events



Seasonal temperature variation
(Taniguchi, 1993)

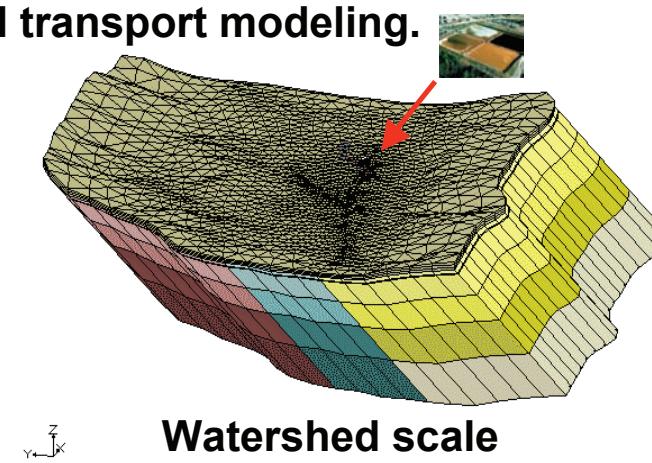
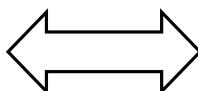
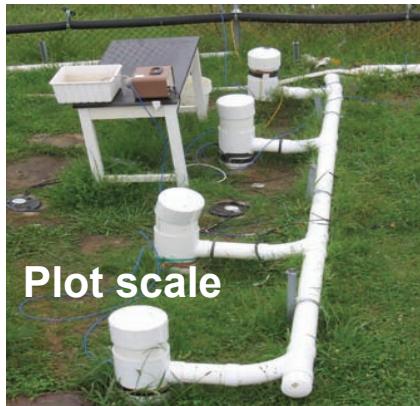


Preliminary Hypothetical simulation



Planned Modeling Efforts:

- Calibrate and test soil titration model for different materials at the site (i.e., gravel fill zone)
- Set up local-scale model to perform simulations for planning and analysis of field-scale pH manipulation experiments
- Implement microbial kinetics and perform initial sensitivity analyses
- Advance multi-scale research on coupled hydrological and biogeochemical processes with computational studies that improve the understanding of controlling mechanisms at the molecular scale and lead to the success of the confluence of molecular-scale processes with field-scale behavior.
- Continued modeling of subsurface heat transfer processes using heat as a tracer to investigate groundwater recharge and discharge.
- Watershed level coupled processes fate and transport modeling.



Materials
Saprolite
Gravelfill
Trench
Transition
High permeable
Conasauga 1
Conasauga 2
Conasauga 3
Conasauga 4
Conasauga 5
Nolichucky 1
Nolichucky 2
Nolichucky 3
Nolichucky 4
Nolichucky 5
Maynardville 1
Maynardville 2
Maynardville 3
Maynardville 4
Maynardville 5